

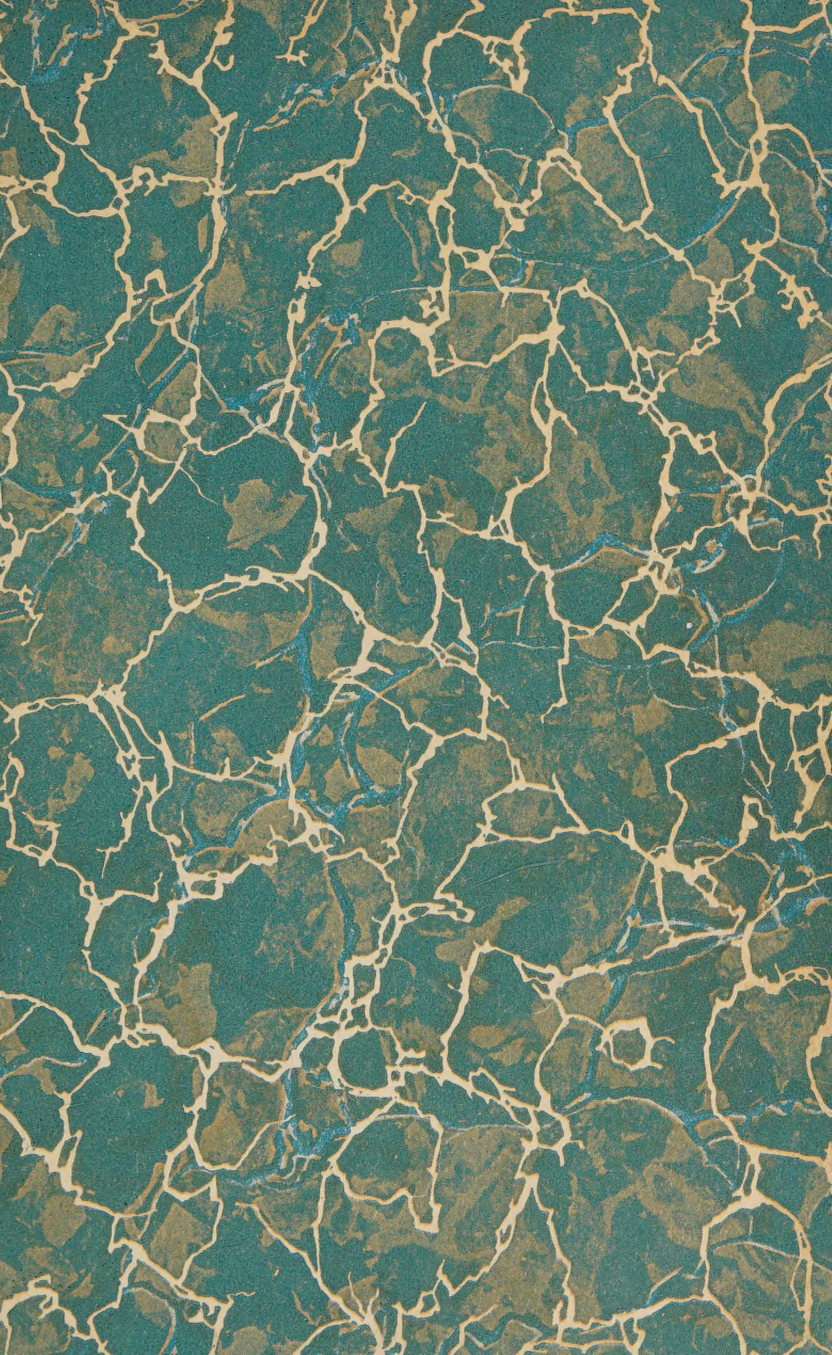
REFINING OF
LIGHT AND
HEAVY OILS



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The image shows the front cover of a book. The cover is decorated with a marbled paper pattern featuring a complex, organic design in shades of teal, brown, and cream. A rectangular white label is centered on the cover, containing the name 'Phineas S. Barium' in a black, gothic-style font.

Phineas S. Barium





Refining of Light and Heavy Oils

By

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CONSULTING PETROLEUM CHEMIST AND LUBRICATING ENGINEER

REFINING OF LIGHT OILS
REFINING OF HEAVY OILS

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REFINING OF LIGHT OILS

Serial 2291

Edition 1

PETROLEUM REFINING

GENERAL REMARKS

1. Introduction.—The petroleum refiner separates the crude oil into its various constituents, principally by the application of heat, and then further purifies the different parts, or *fractions*, into which the crude petroleum has been separated, by the continual removal of objectionable impurities until the different products have been made marketable. These finished products then reach the consumer in such forms as gasoline, kerosene, gas oil, lubricating oil, fuel oil, etc.

2. Types of Refineries.—The type of refinery in operation in any locality will depend on many variable factors, among the most important of which are the kinds of finished products for which there is the greatest market demand, and the type of crude oil being refined.

Refineries in the United States may be grouped as topping plants; skimming plants, with or without a cracking plant; and complete refineries, with or without a cracking plant, operating on paraffin-base crudes, mixed-base crudes, or asphalt-base crudes, and producing both light distillates and lubricants.

Generally, the term *topping plant* means a refinery employed primarily for the production of fuel oil. *Skimming plants* are refineries in which only the lighter fractions from crude

petroleum are removed, no products being manufactured from the heavy residues. Occasionally, however, some skimming plants that operate on a very high grade of crude oil, sell the residuum obtained as the result of distillation, as an untreated cylinder stock, instead of as fuel oil, and thus increase their margin of profit. Usually, skimming plants produce only gasoline, naphtha, kerosene, gas oil and fuel oil. The terms topping plants and skimming plants are sometimes used interchangeably; however, the name topping plant seems to be more in accord with California usage, while the term skimming plant is in wider use in the Mid-Continent oil field.

3. Location and Selection of Refinery Site.—The location of an oil refinery depends largely on the crude oil supply; markets for refined products; and the freight rates on finished products. In the selection of a site for a permanent refinery of fairly large size, the following factors must be considered:

Since rail transportation is important, a site reached by two or more competing railroads is preferable. If crude oil or refined products are to be transported by water, the channel and navigation facilities should be investigated. A minimum depth of channel of 30 feet at low water is recommended.

A surface sloping gradually to a navigable stream or bay, if ocean transportation is desirable, or to a lake or river of substantial size, represents a suitable condition for a refinery site. For most convenient track arrangements, railroad facilities should enter the site at the end farthest from the water.

A soil of sand, loam and gravel is usually suitable for all normal refinery soil loads. Where the bearing power of the soil is questionable, a subsurface survey and bearing test should be made before the refinery site is definitely selected.

The problem of supplying the refinery with water is of extreme importance in determining its location. The quantities of water required will vary with the type of plant: for a complete refinery, approximately 500,000 gallons of water per 24 hours is needed for each 1,000 barrels of crude oil refined. Clean, soft water is required for use in boilers; otherwise, the water must be chemically treated. Water not so pure

may be used satisfactorily for condensers, for fire-fighting, and for general purposes around the refinery. Sea water corrodes equipment and, hence, is not suitable for use. Nearly all refineries use cooling towers or spray ponds to cool water from the condensers, so that it can be reused quickly,

Good drainage conditions are necessary in a refinery site, since, in addition to the disposal of rainfall, consideration must also be given to getting rid of a large amount of condenser water and refinery waste, the latter consisting of slop oils and chemicals. Most slop oil is recovered by means of suitable traps, but the chemicals will pollute streams, and for this reason drainage into small streams should be avoided.

4. Area Required for Refinery Site.—Because of the various stages to which the refining process is carried, no definitely-established rule can be laid down as to the area required for a refinery site. Approximately, however, skimming and topping plants occupy about 5 acres of land for each 1,000 barrels of crude oil put through the plant, and for the same through-put, complete refineries require 10 to 12 acres. In both cases the figures given are exclusive of storage space for crude and finished stocks. Enough storage should be available to hold two or three months' supply of crude oil and the storage for finished stock should be sufficient to take at least three months' yield. Crude-oil storage in 55,000-barrel tanks meets Underwriters' requirements when the tanks are arranged on the basis of 9,500 barrels of storage per acre. A capacity of 20,000 to 25,000 barrels of tank storage per acre is a fair amount for storage of finished stock.

5. Arrangement of Refinery.—No two refineries are arranged exactly the same, and only a general idea as to what, fundamentally, is good practice can be given here. Since the heart of every refinery is the power and boiler house, modern refinery construction favors the practice of centrally locating these units. For general convenience, mechanical shops, storehouse, and laboratory, also should be near to the center of the plant proper. Allowances should be made for future refinery expansion by designing for the largest plant for which any

probable need can be foreseen. Original installations of all departments should be adjacent and compact, with provision made for outward growth. Pressure stills and departments for treating gasoline should be at such a distance from the rest of the plant as to eliminate the possibility that a fire in either may endanger other manufacturing facilities.

PROCESSES AND EQUIPMENT USED IN PETROLEUM REFINING

DISTILLATION PROCESSES

6. Classification of Distillation Methods.—Crude oil is a mixture of hydrocarbons, each of which has a characteristic vaporizing temperature; that is, each will boil at a different temperature. Due to this fact, by the application of heat, or by distillation, as it is more commonly called, it is possible to separate crude oil into different portions or fractions, which, because of their characteristics and usefulness, constitute marketable products more valuable than the original crude petroleum. Only a relatively low temperature is needed to drive off the lighter fractions of the crude oil in the form of vapors; a higher temperature, for the next heavier fractions; and so on until all, or as much of the crude oil as is desired has been distilled.

Distillation may be carried out at atmospheric pressure, under a pressure higher than atmospheric, or under a pressure less than atmospheric. In the most cases crude oils are first distilled at atmospheric pressure. Distillation at higher pressures is a practice followed in the manufacture of gasoline by any of the pressure "cracking" processes. Distillation under diminished pressure is a method used by some refiners in the manufacture of lubricating oils.

In addition to that method of distillation in which fire alone is used as the source of heat, distillation may be further classified according to the means used to accelerate the process, as steam distillation, combined fire-and-steam distillation, combined steam-and-vacuum distillation, and fire distillation, together with the further aid of inert gases or other media.

7. Fire Distillation.—The use of direct fire to heat a still containing the product to be volatilized, is one of the oldest and simplest methods of distillation. However, except in cracking stills, it is not feasible to heat petroleum oils above a temperature of about 500° to 550° F., with external fire heat alone; since the petroleum hydrocarbons will decompose, and products of inferior quality will result. The temperature to which oil may be heated depends greatly upon the type of oil being distilled. Asphalt-base crudes decompose at the lowest temperatures; mixed-base oils, next; and paraffin-base crude petroleum at the highest temperatures. The same is true of refined or semirefined products made from each of these crudes.

8. Units of Heat Transfer.—In processes of distillation, heat is required for two purposes; namely, to heat the liquid from its original temperature to the temperature at which it will distill over, and to change the liquid into a vapor at the boiling point without any increase whatsoever in the temperature of the liquid or vapor. Both of these heat quantities are definite for any give case. Both can actually be measured either in calories or British thermal units.

A *calorie* is the amount of heat required to raise the temperature of one pound of water through one degree Centigrade. A British thermal unit (abbreviated B. t. u.), which is the unit most used in the United States, is the quantity of heat required to raise the temperature of 1 pound of water through 1 degree Fahrenheit. The *specific heat* of a substance is the number of British thermal units required to raise the temperature of 1 pound of that substance 1 degree Fahrenheit. Comparison of the definition of specific heat with that of a British thermal unit, shows that the specific heat of water is 1. Petroleum hydrocarbons vary in specific heat from .4 to .6, the value .5 usually being taken as an average value for a mixture of various hydrocarbons. The *latent heat of vaporization* of a liquid is the number of British thermal units required to evaporate 1 pound of that liquid. For water, the latent heat of vaporization is 970, but 125 is a fair average for petroleum hydrocarbons. However, the latent heat of vaporization for oil varies from about

160 to 50. The higher the boiling point of the mixture of the hydrocarbons being distilled, the lower the latent heat of vaporization.

9. Heat Losses.—The transfer of heat works both ways. Thus, if a pound of oil is heated from 80° to 200° F., the temperature is raised 120 degrees; and, the specific heat of the oil being taken as .5, the heat required to accomplish this is $120 \times .5 = 60$ B. t. u. Likewise, when it cools from 200° to 80° F., it gives off 60 B. t. u. So, too, if, in evaporating, 1 gallon of kerosene, weighing 7 pounds, absorbs 125 (latent heat of vaporization) $\times 7$ (pounds), or 875 B. t. u., it will give off exactly the same number of B. t. u. in condensing to a liquid.

In fire distillation, heat is applied directly to the still by the burning of a fuel, which, in petroleum refineries, is usually either fuel oil or gas. The heat thus generated is dispersed through the bottom of the still to the oil. In practice, some loss of heat results from absorption by the brickwork of the setting of the still, by radiation into the surrounding atmosphere, and by passing out of the stack in the flue gases.

10. Steam and Fire-and-Steam Distillation.—Although in some refineries certain fractions from the crude oil are redistilled by the introduction of steam directly into the oil, the distillation being carried out in so-called steam stills, the more common practice is to distill the oil by a combined fire-and-steam distillation. By this method the still is externally heated by direct fire, while at the same time steam is introduced into the body of the oil through a perforated coil at the bottom of the still.

The fundamental purpose of steam distillation or of a combined fire-and-steam distillation is to distill the oil at a temperature lower than its normal boiling point. With the exception of two refinery operations, namely, the cracking of wax distillate and the removal from crude oil or from a semirefined product, of hydrocarbons of low boiling point, it is of extreme importance in making distillations at atmospheric pressure, that there be plenty of steam in the still in order to minimize the ten-

dency of the oil to decompose. The introduction of steam beneath the surface of a body of oil in a still reduces the temperature required for distillation. The lowering of the normal boiling point of a petroleum hydrocarbon causes it to distill over at a lower temperature than normal, and thus reduces the tendency of the oil to decompose. The introduction of steam beneath the surface of the oil also agitates the oil in the still and thereby minimizes local superheating and cracking. It also speeds up the rate of distillation by increasing the exposed surface of the liquid and by carrying over entrained vapors mechanically. This is because the surface of each steam bubble, passing through the oil, serves as an addition to the effective evaporating surface. If highly superheated steam be used, that is, steam having a higher temperature than that of the liquid being distilled, the steam itself serves to apply additional heat to the oil and, thereby, further increases the rate of distillation.

11. Theory of Steam Distillation.—The injection of steam into oil in a still lowers the distillation temperature by reason of a principle known as Dalton's Law of Partial Pressure. According to Dalton's Law, when two or more gases are confined to a space, each gas or vapor exerts the same pressure as if it alone occupied the entire container. The total pressure, then, is equal to the sum of the partial pressures of all the gases and vapors in the container. For example, assume that there are two receptacles of the same size, one containing oxygen and the other, hydrogen, each at a pressure of 15 pounds per square inch. The two containers are then connected and all the gas is forced from the one into the other. The mixed gases now occupy the same volume as was formerly occupied by only one of the gases, but the pressure is now 30 pounds per square inch. However, the partial pressure of either gas is still only 15 pounds per square inch.

12. In the ordinary straight fire distillation of an oil, the partial pressure of the hydrocarbon vapors, occupying the space in the still above the surface of the liquid at any time after the air originally present in the still has been expelled, obviously is equal to the total pressure in the still. Consequently, the tem-

perature at which any particular hydrocarbon fraction will distill over will be the temperature at which the vapor tension of the fraction is equal to the atmospheric pressure. In steam distillation or in combined fire-and-steam distillation, on the other hand, the partial pressure of the oil vapors in the vapor space of the still is equal to the proportion borne by the volume of oil vapors to the volume of oil vapors plus volume of steam.

Thus, if the total pressure in the still is 20 pounds per square inch and there is present one part of oil vapor to three parts of steam, then the partial pressure of the oil vapors is 5 pounds per square inch. In such a case, the distillation temperature of the oil is that at which the oil's vapor tension is 5 pounds per square inch. *Saturation* of a space above a liquid with the vapors of that liquid exists when the partial pressure of the vapors in the space is equal to the vapor tension of the liquid. At this point, just as much vapor is passing back into the liquid state as there is liquid being vaporized, as a result of which an equilibrium is formed between the vapors and the liquid.

13. The per cent. of vapor that at any given temperature can be contained in the atmosphere above a liquid is equal to the vapor tension of the liquid at that temperature, times 100, divided by the pressure of the atmosphere above the liquid. When a saturated vapor is compressed, the increased pressure forces the vapor to occupy a smaller volume, as a result of which the pressure of the vapor against the surface of the liquid is increased. However, the temperature and, therefore, the vapor tension of the liquid remains unchanged and, as the pressure of the vapor in the space above the liquid cannot remain higher than the vapor tension of the liquid, the vapor will condense out of the atmosphere until equilibrium is again established. A supersaturated atmosphere exists when the per cent. of vapor contained therein is greater than that warranted by the vapor tension of the liquid. This is an unstable condition.

14. **Distillation Under Reduced Pressure.**—One of the methods employed to cause liquids to boil at temperatures lower than their normal boiling points, is distillation under reduced or diminished pressure, or as it is commonly called, vacuum

distillation. Vacuum distillation of an oil means that the pressure on the oil being distilled is lower than atmospheric pressure. It does not mean that there is a perfect vacuum above the liquid. In order that oil or any other liquid may boil, in other words, that distillation may take place, the vapor tension of the liquid being distilled must be a little greater than the pressure above it. When the vacuum during distillation is increased, that is, when the pressure above the liquid is reduced, the boiling point is lowered and a reduction, also, takes place in the vapor tension of the liquid being distilled. Vacuum distillation reduces the tendency of the oil undergoing distillation to decompose, saves fuel, and lessens the amount of condensing and cooling surface required.

15. Other Methods of Distillation.—In distilling the heavier hydrocarbon fractions with steam, it is frequently found advantageous to combine the use of some vacuum. Advantages of this combination lie in the fact that mechanical difficulties incurred in high-vacuum distillations are eliminated, and the passage of the steam and oil vapors from the still to the condenser is accelerated by the use of some vacuum.

Introducing air into the oil, and at the same time maintaining the desired temperature with direct fire heat against the bottom of the still, is a method widely used in the manufacture of artificial asphalt. By this method, the oxygen in the air reacts chemically with the oil.

Distillation with hydrocarbon gas is a method sometimes used but not extensively followed in the United States. Gas distillation is economically feasible only in refineries having an abundant supply of inexpensive gas, and where the boiler water is either of inferior quality or cannot be obtained in sufficient quantities. Distillation with oil vapors is practiced only in exceptional cases, such as when it is desired to blend intimately several kinds of distillates.

STILLS FOR PETROLEUM

16. Classification of Stills.—Distillation of petroleum is accomplished by the use of stills, which may be classified as follows:

1. Shell stills operated at atmospheric pressure.
 - (a) Fire stills. Stills of this type are invariably fitted with a steam coil for making combined fire-and-steam distillations.
 - (b) Steam stills.
2. Pipe stills operated at atmospheric pressure.
3. Shell stills operated under vacuum.
4. Pipe stills operated under vacuum.
5. Stills for distillation under pressure, that is, so-called pressure stills.

17. Shell Stills.—Shell stills have been used extensively in the American petroleum industry for many years. However, for certain uses, particularly for primary distillations of crude oil, they have largely been replaced by pipe stills, but there are many uses for which the shell still is well adapted.

Shell stills are cylindrical in shape, somewhat like a boiler, and are made of strongly riveted heavy steel plates. They are usually suspended in a horizontal position on lugs from columns resting on concrete piers. Thus the still is independent of the brickwork. Stills should be set at a minimum height of 7 or 8 feet above the grates or burners, since combustion is incomplete when they are set lower than this. Such stills vary greatly in size, and they may be as large as 40 feet in length by 14 feet in diameter. Generally, the length of a shell still is approximately three times the diameter. On the top of all horizontal stills is a cylindrical dome, usually equipped with safety devices. To the dome is attached a pipe known as a vapor line. This pipe may be connected either to fractionating towers or directly to the cooling coils in a condenser box. The common practice, particularly with stills that are to be used for distilling both light and heavy oils, is to equip the still with towers; but provision is made for by-passing the vapors directly to the condenser coils when desired.

Some shell stills are made with internal flues. These flues, 4 to 6 inches in diameter and twenty to thirty in number, are placed in the lower half of the still and are so spaced that all are below the normal oil level. With this construction, the

products of combustion after passing under the still are returned through the flues, and the larger heating surface increases greatly the efficiency and capacity of the still.

In the batch distillation of oil in a shell still, the still is filled one-half to three-fourths full of oil. Heat is then applied by a fire under the still, or by either open or closed (or both) steam coils within the still; or by both external direct fire heat and internal steam heat. Heating is continued until all the desired products have distilled over. The residual oil, called "bottoms," is then pumped out, after which the still is recharged with fresh oil.

18. Steam Stills.—In the earlier days of the refining industry so-called steam stills, which are a type of shell still, were largely used in rerunning naphtha, kerosene stocks and other light distillates. Although the use by refiners of efficient fractionating towers on their stills is making rerunning decreasingly less necessary than formerly, nevertheless there are yet some refiners who have not done away entirely with this type of still.

In steam stills, distillation is effected entirely by steam. Closed coils are placed in the bottom of the still, along with open steam sprays. Batch, semicontinuous or continuous operation of either a single still or a battery of stills is possible. Such stills are usually equipped with a combined scrubbing and dephlegmating tower. Bubble towers are used on steam stills by some refiners. In either case, the oil feed enters the top of the tower and trickles down through the baffling material contained in the tower. Thus the descending liquid meets the ascending vapors and steam, and these condense and carry back to the still the heavier fractions. Few steam stills are now constructed by refiners. Formerly, stills for rerunning were usually of the fire-still type, with provision made for conducting combined fire-and-steam distillations. Pipe stills are now used with success by some refiners in rerunning light distillates when redistillation is needed.

19. Rate of Distillation.—The rate of distillation in the shell type of still depends largely on the area of the evaporating surface, the heating surface and the vapor outlet.

In the batch operation of the usual type of shell still, the evaporating surface may be taken as two-thirds of the still diameter multiplied by its length. Thus operated, 1.5 gallons of oil distilled overhead per hour per square foot of evaporating surface is a fair average. In the so-called continuous operation of shell stills, a capacity of 2.5 gallons of overhead distillate per hour per square foot of evaporating surface is a fair figure for use in making calculations. When stills are operated continuously, the level of oil in the still is almost steadily maintained at a point where the still is about half-filled; consequently, length of still times the diameter gives the actual evaporating surface and the factor two-thirds need not be used.

20. In order to effect distillation, ample heating surface must be provided in order to transfer sufficient heat to the body of oil. In continuous batteries of stills, the full half-circumference of the still is often heated, but with batch stills only about one-third of the circumference is directly heated by fire. Reducing the area of the bottom of the still exposed to the furnace gases avoids the possible exposure of part of the bottom to the action of heat on one side without any oil to conduct the heat away on the other. Such a condition would arise in batch distillation unless the protecting walls of the still setting were drawn in toward the center of the still.

The vapor outlet of the still is usually placed from one-half to two-thirds the distance from the fire-box end to the rear. The vapor pipe must be of such area as to permit the oil vapors and free steam, if any is used, to pass freely to the condenser coils, and at such a rate as will accommodate the full still capacity. A vapor outlet area of about .18 square inch for each gallon of oil taken off as an overhead distillate per hour is a fair figure for ordinary calculations.

21. **Pipe or Tube Stills.**—The modern pipe or tube still of simple design consists of a continuous coil of pipe set in a combustion chamber and directly fire-heated. The coil discharges into a large chamber, placed in either a vertical or horizontal position, termed the separator, which must be of ample capacity to permit the free escape of vapors. Tube stills are

sometimes operated in conjunction with a shell still, in which instances the latter serves the purpose of a separator. In the separator the vapors evolved during heating are released, being led first into fractional condensing columns and then, when necessary, through water-cooled condenser coils.

Pipe stills are used at atmospheric pressure, under pressure, and under a vacuum. Their ability to pass oil through a heated zone at high velocity has been the reason for their success. With the earlier designs, carbon soon deposited on the interior of the tubes, necessitating a shut down after a relatively short period of time. But this trouble has been eliminated by the high speed of the oil which carries the carbon in suspension into the separator, where it is drawn off with the residual oil. In passing through a tube still, the stream of oil being heated travels at a definite rate of speed, controlled positively by charging pumps, and gradually increases in velocity as the hotter tubes of the still are reached. This increase in velocity is due to an increase in volume which, in turn, is due to the increase in temperature and to the formation of vapor bubbles in the oil stream. These bubbles increase in size as the tube still outlet is approached, due to the reduction of head pressure. Consequently, the greatest velocity of the heated oil is reached at the tube-still outlet after it has passed through the hottest tubes. A high velocity is necessary, not only to insure a thorough mixing and resultant uniform heating of the oil stream, but also to insure the absorption of heat in the shortest possible time of contact with the heating surface and thus avoid any chance of cracking or decomposition of the oil.

22. A tube still very closely resembles an ordinary water-tube steam boiler in appearance and the operation of each is closely similar. In tube stills, excessive furnace temperatures are avoided by so locating the heating surfaces that they are exposed directly to the fire, but are out of the path of furnace gases. Surfaces thus located absorb heat which is radiated to them but are not overheated. The proper furnace volume and extent of radiant-heat absorbing surface are governed by the quantity of fuel burned. In most tube stills, the furnace

gases before reaching the main flue pass over a bank of tubes, so arranged that the flow of oil through the tubes of the heating surface is counter-current to the flow of furnace gases passing over the outside of the tubes. Consequently, the furnace gases just before entering the flue are in contact with the tubes that carry the entering oil, which is at the lowest temperature, thus cooling the gases to the greatest extent possible. In some cases, the temperature of the oil entering the still is so high that the resultant gases of combustion enter the flue at 700° F. and above. In such instances air-preheaters are employed, by the use of which the air supplied to the furnace is heated by the heat recovered from the hot flue gases. These gases can thus be cooled to 300°-350° F., resulting in a thermal efficiency of the tube still and preheater of 85 per cent. or more. Coils used in pipe stills ordinarily are constructed from pipe ranging from 2 to 6 inches in diameter. Pipe-still distillation units having a maximum through-put of 10,000 barrels of oil in 24 hours are in use.

The principal advantages of the use of tube stills and accompanying fractionating equipment over shell stills lie in greater thermal efficiency, compactness of equipment and lower operating costs.

DEPHLEGMATING OR FRACTIONATING TOWERS OR COLUMNS

23. Purpose of Dephlegmating Towers.—The object of distilling petroleum is to separate the crude oil into various fractions containing compounds having boiling points that are very close to each other. Crude petroleum consists of hundreds of closely related compounds, the boiling points of which range from ordinary temperatures to very high temperatures. As the oil is first heated in a still, those compounds that have the lowest boiling points will be distilled off first, but at the same time they will be accompanied by a relatively small percentage of compounds that boil at just a little higher temperature.

Dephlegmating, or fractionating, towers or columns are used in connection with the operation of most stills to remove these compounds of higher boiling point, and thus obtain a cut, or

fraction, consisting of compounds with boiling points that are comparatively close together.

The cuts or fractions that are made in the distillation of crude oil are chosen arbitrarily. The range of boiling points in any cut may be either very close or very wide, depending on the nature of the oil, the efficiency of the apparatus and the physical characteristics desired in that particular cut.

24. Most fractionating towers consist of vertical cylinders filled with some material that presents a large amount of surface to the oil vapors as they pass through it. In the earlier types of towers the common forms of material with which such towers were frequently filled were crushed stone, broken up tiling or horizontal, metal plates. A very efficient type of tower that has come into use in the petroleum industry, and is replacing the older, less efficient types, is the so-called *bubble tower*. Such a tower consists essentially of a vertical column filled with plates ranging in number from five to twenty, depending on the size of the tower, with scores of openings in each plate over which bubble caps are inverted, the whole being so arranged that as the vapors pass up through the tower they are forced through successive pools of liquid. In any type of tower, the hot oil vapors from the still enter the tower near the bottom, work their way up through the small spaces between the pieces of baffling material and leave the tower at the top.

The fundamental action of dephlegmation results from the fact that the tower, being cooler than the still, causes those compounds of high boiling points to condense out. The baffling material also tends to remove the mechanically entrained liquid from the oil vapors. Consequently, the hot liquid slowly trickles down over the baffling material counter-current, or in an opposite direction, to the incoming vapors, which slowly bubble up through the hot liquid, and thus the constituents that have higher boiling points are almost completely removed. The liquid that drains out at the bottom of the tower either may form one of the cuts resulting from the distillation, or it may be returned to the still, or it may be circulated over the top of another tower.

25. Factors That Influence Efficient Rectification.—In addition to the necessity of intimate contact between vapor and liquid in a dephlegmating tower, other factors that influence efficient rectification are as follows:

1. Suitable velocities are necessary.
2. Suitable temperatures must be maintained, both at the top and bottom of the column.
3. Minimum gain or loss of heat to or from the column is important. The heat for vaporization, which can enter only at the base of the column, should be conserved as much as possible.
4. Return of reflux condensate (condensed heavier vapors) to the column is best accomplished by cooling the top of the tower rather than by pumping the reflux back to the top. In the ideal column, distillation and refluxing take place all the way up the column, with just the right temperature gradient from top to bottom. In that event there is no need for an artificial temperature drop at the top and for the return of reflux to the tower. But, under such conditions the column is subjected to fluctuating weather changes. Hence, in actual installations, the tower is shortened somewhat, the temperature gradient is sharper, accurate temperature control is maintained and reflux condensate is returned to the column.
5. Distillate that is pumped back into the column should be introduced at a point where the composition of the oil inside the column is the same as that of the oil being introduced.

In addition to the foregoing factors that influence the efficiency of a dephlegmator, it should also be noted that for greatest column efficiency only two fractions should be taken from a tower; these are the overhead cut and the base cut. In column operation a definite temperature gradient establishes itself in the column. In plate columns, the composition of the fluid on a particular plate is definite and different from that on any other plate. When more than two fractions are removed or when oil is introduced indiscriminately, these conditions are disturbed. If such a practice be followed, the column makes an attempt to adjust itself, but this is done at the expense of efficiency.

CONSTRUCTION CHARACTERISTICS OF DEPHLEGMATORS

26. Methods Employed to Secure Efficient Dephlegmation.

A dephlegmator, or fractionating tower, is simply a means for bringing into intimate counter-current contact a stream of liquid and a stream of vapor. This may be accomplished by the use of equipment in which a spray of liquid falls through a current of vapor rising from a still; by the use of a multitubular condenser with vertical tubes down which the condensate runs, the vapor entering at the base and passing up through the tubes. In some installations chains are hung in the tube. Other methods consist in the use of packed towers and plate columns, which may be of the sieve-plate or the bubble-plate type.

27. Packed Towers.—Packed towers or plate columns of either sieve or bubble design are used most widely in petroleum refining; of these, the bubble-plate columns are most favored by refiners. With packed towers, the smaller the sizes of the packing pieces, to a certain practical limit, the more efficient is the tower. Glass rings as small as $\frac{3}{8}$ inch to $\frac{1}{2}$ inch in diameter have been used with success on columns 12 to 18 inches in diameter; but, for columns 24 to 30 inches or more in diameter, $\frac{7}{8}$ inch seems to be the minimum practicable diameter of filling material. The function of the packing in a tower, whether a packed tower or a plate column, is to distribute the vapor and liquid uniformly through the column, to bring the two into intimate contact in a minimum of space, and to break the fluid up into fine particles. Raschig, Lessig and Breaget fillings are the trade names of filling materials that are largely used in packed towers.

28. Sieve-Plate Columns.—The sieve-plate column is ideal for some purposes, but to be successful it has to be built exactly right and be run at a definite rate. As its name implies, the sieve-plate column is made up of perforated plates placed in a vertical tower. The velocity of the vapor passing through the perforations keeps the liquid from running through them and makes it pass across the plate and through overflow pipes. If this velocity is not sufficient, the plate will leak or dump its

load through the perforations. Stills equipped with sieve-plate columns must be run to capacity in order even to approach satisfactory results. This characteristic of columns fitted with sieve plates prohibits their use in cases where the desired capacity is not always the same. Another limitation of sieve-plate towers is the corrosion of the perforations. It takes very little corroding action on a small hole to double its area and, as the area of the hole is increased, the capacity of the tower must be increased.

29. Bubble Towers.—Various designs and modifications of fractionating, dephlegmating or bubble columns or towers are

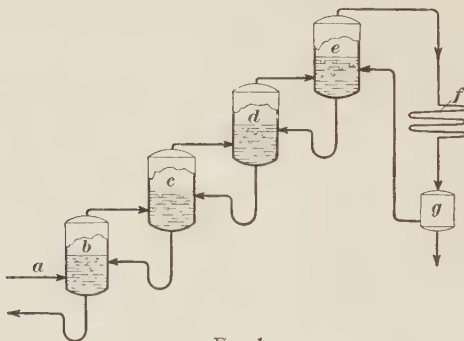


FIG. 1

used in the oil industry. The basic principle involved, however, in all designs is the same, and consists of the stripping action obtained when a hot vapor that contains comparatively low-boiling constituents, is caused to bubble through a liquid that contains higher-boiling constituents which are at a lower temperature than the vapor. The principle of dephlegmation is illustrated by Fig. 1. Thus, if hot oil vapor *a* is introduced beneath the surface of the cooler liquid in the vessel *b*, it will be slightly cooled as it bubbles through the liquid, and a large portion of its heavier constituents will be condensed out and will remain in the vessel. The result is that the vapor leaving the first vessel, will be lighter and will have a lower boiling range than that which enters it. Consequently, as the vapor passes through the remaining vessels *c*, *d*, and *e*, it will become

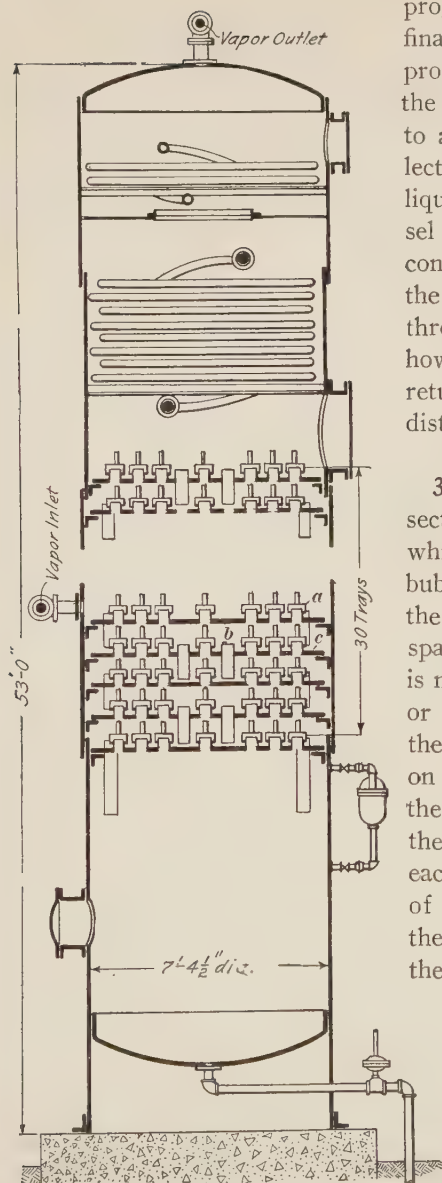


FIG. 2

progressively lighter, until finally, when it possesses the properties desired, it is led to the condenser *f* and converted to a liquid fraction and collected in the receiver *g*. The liquid, or reflux, in each vessel is made up of the heavier constituents condensed from the vapor as it bubbles through. For the last vessel, however, it is necessary to return a small portion of the distillate from the receiver.

30. In Fig. 2 is shown a section of a bubble tower in which the arrangement of the bubble caps *a*, the location of the overflow pipes *b* and the spacing between the decks *c*, is made clear. On each tray or deck is a layer of liquid, the depth of which depends on several factors, such as, the permissible back pressure, the amount of reflux over each deck and the velocity of the vapor. In operation, there is a continuous flow of the vapor upwards through the tower and of the reflux downwards through it. The manner in which the vapors pass through the caps is illustrated in Fig. 3, in which the

caps *a* and *b* are on one deck and caps *c* and *d* on the deck immediately above. The cap *d* is shown in vertical cross-section. The hot vapors, as they pass through the tower, are deflected by the bubble caps and caused to pass downwards in order that they will bubble through the liquid on the plate and then finally escape in the form of bubbles through the serrated edges of the caps. The condensed liquid then overflows through the pipe *e* to the tray below.

31. The bubble tower is considered the most efficient type of tower for use in petroleum refineries. In a study of rectification principles, three important points to be considered are

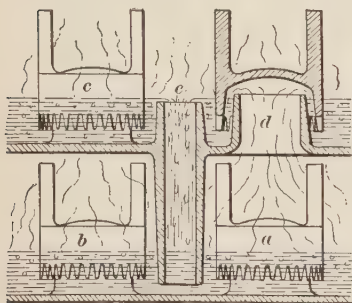


FIG. 3

that it is necessary to have large interfacial surface between the liquid and the vapor, high vapor velocity, and long time of contact. To obtain large surface and high vapor velocity, the orifices through which the vapor flows must be small and numerous, therefore it is a common practice to use a large number of small, circular bubble caps.

To lengthen the time of contact, it would appear that the depth of the liquid on the plate should be increased. However, experience has shown that this has little effect. The reason lies in the fact that, as a vapor bubble rises through a liquid, equilibrium is quickly established between the adjacent films of vapor and liquid. But, diffusion from the vapor comprising most of the bubble, into that part of the vapor composing the film layer, is relatively slow; so slow, in fact, that the time involved cannot be compensated by such increase of the total time of contact as is feasible by increasing the depth of the liquid on the plate. The solution of this phase of the problem lies in disturbing the bubbles of vapor in some mechanical manner. For example, if the bubble caps are spaced closely together, the bubbles of vapor from one will strike the bubbles

from another. This mixing together of liquid and vapor results in effective contacting.

32. Factors That Influence Design of Bubble Towers.

Some of the factors that influence the design of bubble towers are plate spacing, depth of seal, arrangement of bubble caps and position and length of overflow pipes or down-spouts. In practice it is found that caps 4 to 6 inches in diameter, spaced two inches apart, are usually satisfactory. The slots or serrations should be $\frac{1}{8}$ inch to $\frac{1}{4}$ inch wide, $\frac{1}{2}$ inch to 1 inch long, and spaced $\frac{1}{8}$ inch to $\frac{1}{2}$ inch apart. The slots on the edges of the caps must not be too close together, because the metal will be eroded by the rapidly moving vapor. The depth of the liquid above the top of the slots or serrations in the caps need not be greater than 1 inch, and the total depth on the plate not over $1\frac{1}{2}$ to 3 inches. The sections of a column should be of such a height that the distance from the surface of the liquid to the plate above is at least 6 inches. Otherwise, opportunity will not be given for entrained droplets of liquid to settle from the vapor.

Other things being equal, the higher the vapor velocity in the bubble-cap column, the better. But other things are not equal. As vapor velocity increases, entrainment increases and time of contact decreases. However, these changes are not enough to offset entirely the benefits of high vapor velocity. Still other factors enter into the situation. As velocity increases, the resistance to flow also increases. If the velocity is too great, the liquid is lifted from the plates and the column is no longer an effective contacting means. All things considered, a vapor velocity of 10 feet per second is a proper figure to use as a basis for design. A column calculated to operate at this velocity can be greatly overloaded if necessary, yet it is not an unreasonably expensive apparatus with which to start.

When vapor velocity and bubble-cap dimensions and spacing are chosen, the general form of the column is determined. Thereafter, the number of sections in the column is approximated by making use of any available information on the effectiveness of the particular form of plate that is to be used.

The result is that the column will be found to be long and slender, rather than short and broad.

33. Automatic Temperature Control in Fractionating Towers.—For the most efficient operation of any type of fractionating tower, close control of the temperatures of the vapors passing from the top of the tower to the condenser is necessary. A constant temperature in the outlet vapor line from the tower results in the production of a uniform grade of gasoline, kerosene or whatever the light-oil product being made. If the outlet vapor temperatures are low, the condensed gasoline will have a higher end point than desired. This will necessitate a redistillation of the product, with consequent distillation loss, interference of plant routine and generally increased, unit operating costs. If tower temperatures are low, the yield of gasoline, or any other particular product, fractions of which are being removed as an overhead distillate, will be low. This means a reduction in plant output. On the closeness of tower temperature control depends the completeness of recovery of each light-oil fraction. Consequently, modern refinery practice favors the use of some type of automatic device to control the temperature at the top of each tower.

34. Use of Mist Extractors.—Particularly in the distillation of heavy oils, a modification of the dephlegmation principle, in the form of an apparatus known as a mist extractor, is quite extensively used in refineries. During distillation and dephlegmation, a slight drop in temperature will permit the formation of a mist in the vapors; this mist, which consists of the highest-boiling portions of the vapors, is carried along with the lighter vapors. In mist extractors the particles are actually thrown out of the vapor stream and impinged on the rigid walls or plates of the apparatus by increasing the velocity of the vapor stream and at the same time causing sudden and frequent changes in the direction of the stream. Mist extractors are another means of obtaining closer fractions or cuts during distillation.

CONDENSATION AND CONDENSERS

35. Fractional Condensation.—As previously stated, the oil vapors from the still usually pass to fractionating towers, which are in part fractional condensers. From these the path of the vapors lies through water-cooled, cast-iron coils placed in steel condenser boxes, or through the condenser proper. Sometimes, however, the vapor line leads directly to the condenser box. The purpose of a condenser is to cool the vapors coming from the still, to a point where the maximum possible proportion of vapors that is economically feasible will be converted into liquid.

Fractional condensation is a principle extensively practiced in petroleum refining, but it is not nearly so efficient as dephlegmation, especially at fairly high temperatures. Fractional condensers may be either of the aerial, or air-cooled, type, or of the water-cooled type, or they may be simply vapor heat exchangers. In all cases, the purpose of fractional condensation is to obtain a closer cut—that is, hydrocarbons with boiling points more nearly alike—and thus reduce to a minimum the quantity of oil that must be rerun.

36. Principles on Which Condensation is Based.—In order that the hot vapors of the oil being distilled shall condense to a liquid, heat must be removed from them. In other words, for every pound of vapor condensed—that is, every pound of liquid formed by condensation—a definite amount of heat must be removed from the condenser by being absorbed in the surroundings.

When vapor is cooled to a point where it condenses to a liquid, it gives off its latent heat of vaporization; consequently, before condensation can take place, *the condenser must remove a quantity of heat equal to the number of degrees of drop, from the still temperature to the average condensation temperature, multiplied by the number of pounds of vapor and by the specific heat of the vapor.* The specific heat of the vapor is the quantity of heat that must be removed in order to cool 1 pound of vapor through 1° F., which is the same amount required for

raising the temperature of 1 pound of the vapor through 1° F. The average specific heat of petroleum vapor is about .25, it being greater for the lighter fractions and less for the heavier ones.

After condensation has taken place, the condensate is further cooled by its passage through the condenser. *The quantity of heat removed in the cooling is equal to the number of degrees of drop, from the condensation temperature to that at which the condensate leaves the condenser, multiplied by the specific heat of the liquid.*

37. Types of Condensing Apparatus.—The three principal types of condensing apparatus in general use are: Continuous submerged coils; parallel submerged coils; and shell-and-tube condensers.

Practical operating conditions determine the type of condenser that will be most suitable. For all conditions, the continuous coil is the most generally satisfactory and is the more widely used. The parallel coil is more efficient for heat transfer, but it is more difficult to clean. Further, since in this type the coils branch from a common header, velocities of fluids in different pipes are easily altered by changes in surface conditions, and velocity changes are apt to cause plugging of the coil with wax when wax distillate is being separated from the oil undergoing distillation. Such a condition would be discovered at once when continuous coils are used. Consequently, parallel condenser coils cannot be recommended for use with batch stills working on crude oil; but for stills operated as a continuous battery, parallel condenser coils can be employed with the first stills of the battery until the kerosene cut is over, with better results than can the continuous submerged coils. For the rerunning of naphtha or kerosene distillates, the use of the parallel coil is satisfactory and it decreases the amount of condenser surface necessary. The shell-and-tube type of condenser is not used more extensively for the same reasons that limit the use of parallel condenser coils; further, it is not suitable for use under any conditions where the water outlet temperature is above 150° F., unless the quality of the water is above ques-

tion. Otherwise, scale formation on the coils would be a serious matter.

38. Sizes of Condensers.—The size of a condenser is influenced by the length of time allowed for the removal of the heat, the coefficient of transmission of heat, the specific heat of the condenser fluid, and the average temperature difference between the hotter and the colder fluids throughout the entire condenser.

The coefficient of heat transmission is a numerical figure specifying the number of heat units (B. t. u.) that will be transferred from a hot fluid to a colder one through 1 square foot of surface in 1 hour for a temperature difference between the two fluids of 1° F. Depending on conditions, this value may vary from 2 to 100 B. t. u. When the number of B. t. u. that the cooling medium must remove in one hour and the number of degrees that this medium increases in temperature while passing through the condenser are known, it is possible to find, from the specific heat, the number of pounds of cooling medium that must pass through the condenser box in one hour. For approximate calculations, the simple arithmetical average of the difference in temperature between the two fluids throughout the entire condenser may be used in determining the average temperature difference. As an example assume that the oil vapors enter the condenser at a temperature of 580° F., and, after being condensed and cooled, leave at a temperature of 130° F., and that the cooling water enters the condenser at 80° F., and, after flowing counter-current to the oil, leaves at 170° F. The arithmetical temperature difference then is

$$\frac{(580-130) + (170-80)}{2} = 270^{\circ} \text{ F.}$$

In general, the required condensed capacity depends on the quantity of heat that must be removed by the condenser, and the amount of cooling surface and of cooling medium necessary to remove this quantity of heat.

39. Receiving House.—The receiving house, also termed the tail house or running house, is the building to which the lines from each condenser must pass so that the distillate can

be directed to the proper tank. Here all the streams from each still, or each cut from each still, if towers or fractionating condensers are used, pass through individual *look boxes*. These look boxes make possible the ready observation of the stream and provide convenient means for sampling the stream for subsequent physical tests. When the character of the stream reaches the point desired, the oil may be directed to the proper tank by the manipulation of a few valves. Thus it is seen that the entire process of distillation is controlled from the receiving house.

HEAT EXCHANGERS

40. Classes of Heat Exchangers.—For economical operation, it is necessary for the refiner to conserve waste heat wherever possible. Particular advantage is taken of the opportunities offered for making this saving by the addition of suitable heat exchangers to the distillation equipment.

Heat exchangers are generally classified as vapor exchangers and liquid, or residual, exchangers. Vapor exchangers are not used extensively in this country, because their first cost is high, and their heat transfer efficiency is low. Liquid exchangers, however, are in use in almost every refinery operating any continuous distillation process in which the heat is either added to or removed from the products handled.

41. A vapor heat exchanger consists essentially of a cylindrical shell containing rows of pipes, the whole being placed above the level of the still. The oil on its way to the first still of a continuous battery passes through the space around the pipes in the cylindrical shell, while the vapors from the still pass through the pipes in a direction counter-current to the oil that surrounds the pipes, thus heating the oil. Residual-heat exchangers are of the tank-and-coil type, the shell-and-tube type, or they may consist of double-pipe apparatus. These exchangers are used to transfer heat from the hot bottoms, or residue, which is pumped continuously from the last still of a battery or pipe-still unit, to the crude oil or other product that is being charged to the first still. In all cases, the two liquids move counter-current to each other, that to be heated flowing through

the pipes or coils and being surrounded by the other liquid. The important things to be considered in all heat exchangers are that the equipment shall be safe, practical, and such that it will provide sufficient contact surface between the two liquids so that there will be a maximum of heat interchange without undue friction or loss in radiation from prolonged passage.

REFINING OF LIGHT OILS

METHODS OF OPERATING STILLS

42. Light Oils Defined.—By the term light oils is meant those products of lower boiling points that are separated from crude petroleum and, when purified, reach the market in the form of different grades of gasoline, kerosene, naphtha or gas oil, as well as intermediate distillates of various specifications. In other words, light oils include all the more volatile fractions separated from the crude oil before lubricating-oil cuts or fractions are obtained.

43. Methods of Distillation.—Dependent on the type of equipment available for use and the manner in which such equipment is operated, methods of distillation for light oil may be classified as batch distillation, semicontinuous distillation, continuous distillation in shell stills, and continuous distillation in pipe stills. The name given each method indicates the manner in which the operation is carried out.

44. Batch Distillation.—In batch distillation the still is charged with oil until it is about two-thirds full, after which the temperature of the oil is gradually raised, and the distillate that comes over through the condenser is allowed to pass to the proper run-down tank. When, as determined by laboratory tests, the gravity of the distillate reaches a point as previously decided on, a change is made immediately in the manifolds in the receiving house, so that the oil will run into another tank. The number of different cuts that thus will be made before the bottoms, that is, the oil remaining in the still, is also of the desired physical characteristics will depend on what has been found to be most economical and advantageous. When the

residual oil is of the desired tests, it is pumped to the proper storage tank where it is kept until it is converted into other products, such as lubricating oils. Batch distillation is usually conducted by use of both fire and steam, the latter being allowed to enter the still at temperatures ranging from 250° to 350° F. Sometimes, however, it is desired to crack, or decompose to a certain extent, the oil in the still, in which case some refiners use either fire alone or fire with only very little steam during the distillation. Batch distillation is less efficient than other methods, principally because of greater fuel consumption, so that this method of operating stills is not the most economical for the refiner.

45. Semicontinuous Distillation.—In semicontinuous distillation the still is charged with oil, which is gradually heated, and as the more volatile portions distil over, the amount of oil removed in this manner, is replaced by fresh oil pumped into the still. This operation is continued until the still is filled with a heavy oil of the desired tests, after which the charging of the oil is stopped, and the bottoms are pumped out to storage; or this product, with no further additions, may be further reduced in the same still by batch distillation until the residual oil is at the point wanted. By reduction is meant the process by which the lighter fractions are removed from an oil, leaving a residue in the still that will pass certain prescribed physical tests.

Semicontinuous distillation is more efficient and economical than batch distillation, since plant capacity is thus somewhat increased over the batch method.

46. Continuous Distillation in Shell Stills.—Shell stills are often arranged in batteries of from two to twelve stills and operated continuously, with stops only for extraordinary repairs. This is the most common practice, and is the method by which the highest efficiency can be obtained from such stills, as ordinarily equipped.

In all batteries for the continuous distillation of crude petroleum or any of its products, the stills are so arranged that the bottom of each successive still is at a level of 6 to 12 inches

below the preceding one. Furthermore, all stills are connected by flow lines, which allow the liquid to overflow from one still into the next one of the series. Five or six stills to a battery is the arrangement most frequently used by refiners.

When, for example, five stills are being used together for the continuous distillation of crude oil, the oil is pumped steadily through suitable heat exchangers counter-current to the outflowing hot residuum, into the first still of the battery, where the oil is heated to temperatures ranging from 250° to 350° F. The distillate coming off at this temperature passes into the gasoline run-down tank. The bottoms from the first still then flows into the second still, which is maintained at a temperature usually 50° to 100° F., higher than that of the first still, thus distilling off a product of higher boiling point. In a like manner, the oil passes through the third and fourth stills of the battery, the temperature of each being higher than the one preceding, and a certain percentage of distillate is taken off at each point until, eventually, the last still is reached, where the residuum is pumped off continuously to the heat exchangers and then to storage. This still is kept at the highest temperature, and therefore the distillates produced therefrom are the heaviest in gravity.

47. Generally, in the operation of a continuous system, it is never necessary to shut down the entire battery for cleaning or for ordinary repairs. Usually it is possible to isolate the still that needs attention by by-passing the oil stream around it and then distributing the distillation among the remaining stills.

Frequently, in operating a battery of stills under certain conditions on some crude oils, the residuum from the last still of the battery is allowed to flow into one of either two or three additional stills, where the oil is reduced by batch distillation either to coke or to a residuum of certain predetermined physical characteristics. Where three stills are so used in connection with a battery of continuous stills, one still is being charged with oil; the oil in the second still is being reduced to the point desired; while the heavier bottoms in the third still either is being pumped out or, the still is being cleaned.

Continuous distillation is more efficient and gives lower operating costs than any other method of distilling oil in shell stills, more especially crude oil, both from the standpoint of fuel economy and plant capacity. This is because the same conditions of operation are steadily maintained, heat losses by radiation are lessened, maintenance costs are lower, and, in general, there is a greater efficiency both of fuel and of labor.

48. Continuous Distillation in Pipe Stills.—Continuous distillation in pipe stills is gradually replacing other methods of operating stills, particularly in the primary distillation of

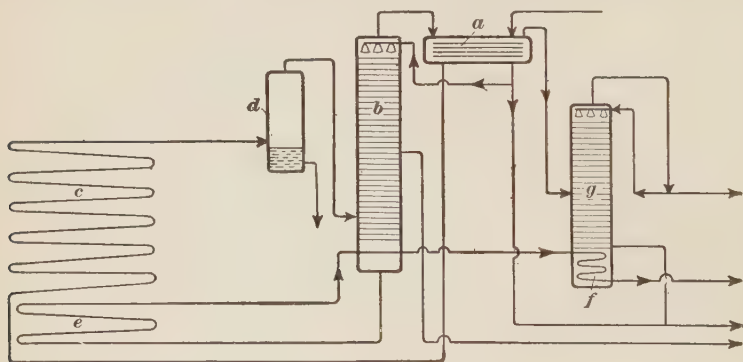


FIG. 4

crude oils. This is because such distillation units give lower unit operating costs than do any others. There are almost as many different designs of pipe-still units and methods of operating them, as there are refiners utilizing such stills. Consequently, a description of the method of operating a particular pipe still must be considered as being indicative only of the practice followed by refiners in general.

In Fig. 4 is shown a layout of the equipment used in a pipe-still distillation unit which has a capacity of 3,500 to 4,000 barrels of mixed-base crude oil per day, and yields about 60 per cent. of the total charge in three overhead products, namely, gasoline, kerosene, and gas oil. The gasoline and kerosene require only slight chemical treatment before being marketable. Also by a slight modification of the ordinary procedure, it is

possible to obtain in a single operation from this distillation unit the so-called export gasoline, which has an A. P. I. gravity of 64° – 65° , as well as the usual gasoline product of 437° F. end point.

As shown in Fig. 4, the crude oil enters the system through a vapor heat exchanger *a*, where its temperature is raised to approximately 225° F., by the vapors from the top of the first bubble tower *b*. It then enters the pipe still *c*, each unit of which contains 154 tubes, 4 inches in diameter and 20 feet in length, arranged in a furnace in the form of two coils. The vapors leave the pipe still at 600° to 650° F., and pass into an evaporator, or expansion chamber *d*, and then to the bubble tower, which is entered at one of the lower plates. About midway up the tower the kerosene fraction is withdrawn. From the bottom of the tower, which is at a temperature of about 600° F., a portion of the gas oil is withdrawn and further heated by passing through the reboiler coil *e* in the furnace. It is then returned to supply additional heat at the bottom of the bubble tower, thereby serving to obtain close fractionation between the end point of the kerosene and the initial boiling point of the gas oil. The remaining gas oil flows through a closed coil *f* in the base of the second bubble tower *g*, where it provides additional heat for fractionation, and finally passes through cooling coils to storage.

The gasoline vapors that leave the top of the bubble tower *b* are at a temperature of about 360° F., and, as these pass through as reflux at the top of the bubble tower *b*, the temperature of the crude oil, a portion of the vapors is condensed into gasoline. The uncondensed gasoline vapor passes off into the second bubble tower *g* where it is fractionated into gasoline having an end point of 437° F. and an export gasoline, which has a higher gravity and a lower end point than does gasoline intended for general consumption in this country. The export gasoline is withdrawn from the top in vapor form and the usual gasoline fraction is condensed and withdrawn at the bottom. The condensed gasoline from the vapor heat exchanger is partly utilized as reflux at the top of the bubble-tower *b*, the temperature of the gasoline vapors being automatically regulated and controlled

by the amount of reflux being pumped over. In order to obtain the necessary end point on the export gasoline, a portion of the condensed product is refluxed over the top of the bubble tower *g*, the quantity being regulated, as in the first tower, by automatic temperature controls. Electrically operated instruments of the potentiometer type are used to record temperatures at various important stages in the process, while the control of fractionation is by temperature-regulating devices that automatically control the rate of reflux material at the top of the bubble columns. Charging and transfer pumps, which are housed beneath the condensers, are controlled by automatic float valves. The hot residuum from the topping plant or evaporator *d* is passed directly to the reducing stills.

DISTILLATION OF PARAFFIN-BASE CRUDE OILS

49. Fire and Steam Distillation.—Paraffin-base crude oils are usually distilled by a fire-and-steam distillation, either in horizontal shell stills or by fire distillation in pipe stills, or in distillation units in which the use of shell and pipe stills is combined. The so-called cracking distillation of paraffin-base crude oil itself in ordinary shell stills, is not practiced any longer, although this method of distillation is sometimes applied in redistilling certain particular cuts from the crude.

Continuous distillation in a battery of horizontal shell stills was formerly the most general practice in the distillation of crude oil among refiners in the Appalachian region. Now, however, refinery technology favors the use of pipe stills.

To make more easily understood the manner in which paraffin-base crude oils are separated into various marketable products, distillation in shell stills will be assumed and, further, that such stills either are not equipped with fractionating towers, or else with towers of such design that close fractionation of the overhead distillates is not obtained.

50. The number of stills that are arranged into a battery so as to operate continuously will depend on practical conditions in the plant itself. The use of five stills in one battery, with two or three other stills for batch distillation so connected

together that the bottoms from the fifth still of the battery can pass to one of the batch stills to be further reduced, represents an arrangement long favored by refiners. The gravity of the distillate from each still and the nature of the cut will depend on the temperature maintained on that still, and the temperature, in turn, will depend on the products desired, the kind of crude being run, and what previously has been determined as the best procedure and method of operation on that particular crude.

Regardless of whether or not the crude is being run in continuous, semicontinuous or batch stills, in the fire-and-steam method of distillation, steam is allowed to enter the still when the temperature of the oil is sufficiently above the boiling point of water so that the steam will not condense in the still. The temperature of the oil at the time when the steam enters the still will vary from 250° to 350° F., depending on the degrees of superheat of the steam. The presence of steam in the still insures the distillation of the oil at a much lower temperature than when fire alone is used, and prevents the decomposition, or cracking, of the compounds of higher boiling points, which are valuable for lubricating stocks.

51. In batch distillation, using fire and steam the oil is charged into a horizontal, cylindrical still until the latter is two-thirds to three-quarters full. Firing of the still can be started while the oil is being pumped in. Benzine, or crude naphtha, is the first product to distil over. Later this is treated and rerun for various grades of gasoline. Depending on the efficiency of the equipment and the operating practice favored, cuts for gasoline can be made directly from the primary distillation of the crude, and a benzine cut can be made after some of the gasoline has thus been removed.

The stillman controls the process of distillation by noting, with a hydrometer, the gravity of the liquid flowing through the look-box. When a benzine cut is being made, the stream is allowed to pass into the same run-down tank until the gravity of the stream is from about 48 to 50°, by a hydrometer that is graduated in the A. P. I. scale. The exact point at which

the run-down tank will be changed and the kerosene-distillate cut obtained will depend on what has proved to be the most advantageous practice in that particular plant for the crude being run. From 30 to 45 per cent. of the total crude charged to the still thus may be collected in one tank as a benzine or naphthà cut.

The kerosene-distillate cut is collected until the gravity of the stream is from 42° to 38° A. P. I. This, however, also depends on economical plant practice. The kerosene-distillate likewise is rerun to make the various grades of marketable kerosene. The yield of kerosene distillate will vary from 15 to 30 per cent., depending on the kind of crude, manner and efficiency of operation, and market demand for the finished product.

52. Gas oil is the product that distils over after the kerosene-distillate cut has been taken off. The distillate is allowed to flow into the gas-oil tank from the time at which the kerosene-distillate fraction ceased to flow until there is a showing of appreciable quantities of wax in the liquid flowing through the look-box. At this point the gravity of the stream will be about 35.5° A. P. I. The yield of gas oil will be from 10 to 20 per cent. of the crude. If a poor separation of lighter fractions has been obtained in distilling off the gas oil, and if it is economical to do so, this product is rerun, being further reduced with fire and steam, and a small yield of kerosene distillates is obtained therefrom. However, those refiners who have cracking plants installed for increasing gasoline yield usually use the gas-oil cut as the charging stock for pressure-still cracking plants.

53. Wax distillate is the name applied to the product that follows the gas-oil fraction. It is this cut that is the starting point for the manufacture of the lighter-bodied lubricating oils. The wax-distillate cut is collected, in one tank, from a stream-gravity of about 36.5° down to about 32° A. P. I. The extent of the distillation, and hence the lowest point reached in taking off the wax distillate, will depend on what physical characteristics are desired of the residuum (or steam-refined cylinder

stock, by which name it is better known) remaining in the still. There is a market demand for steam-refined cylinder stocks of 600°, 635° and 650° F., fire test, and also for cylinder stock of 600° F., flash test, so that the point to which the crude is reduced depends primarily on the grade of stock which the refiner finds he can sell most readily, and on which he can make his greatest profit.

The yield of wax distillate may comprise from 15 to 30 per cent. of the crude; and the percentage of cylinder stock may vary from 10 to 20 per cent.

54. If a light-gasoline fraction is made directly from the crude oil, this gasoline may or may not be treated chemically in either a continuous light-oil treating plant or in light-oil batch agitators, depending on whether or not such treatment is necessary.

When a benzine cut is made from the crude, it is usually either rerun at once in steam stills and the different grades of gasoline and naphtha are treated chemically, if necessary, after rerunning; or the crude benzine is treated with sulphuric acid, washed with water, treated with caustic soda, and again washed with water, all either in continuous or batch agitators, before the oil goes to the steam stills for rerunning.

The principal grades of gasoline and naphtha for which the refiner of paraffin-base crudes finds a ready market have an A. P. I. degree reading ranging from 58° to 72° for gasoline and from 52° to 56° for naphtha.

The bottoms remaining in the still, after the benzine or crude-naphtha cut is rerun, is pumped to a rerun distillate tank. When a sufficient quantity of this residual oil has accumulated, it too is rerun, and cuts are made on the overhead distillate for benzine and kerosene distillate, and the residual oil is pumped to the fuel-oil storage tank.

The kerosene-distillate cut made in the primary distillation of the crude oil is rerun either in steam stills using steam alone for heat, or in fire stills using both fire and steam in the distillation. This fraction is reduced in either type of still until the oil is of the proper flash and fire test. The grades of burn-

ing oil produced and the characteristics of the distillates resulting from the rerunning of the kerosene-distillate cut will depend on the manner in which this cut was made in the distillation of the crude oil.

55. In the foregoing, it has been assumed that the batch distillation method was employed, the separation of the different fractions not being close. In the operation of a continuous battery, however, the oil in each still is kept at such a temperature that a particular product will be separated as an overhead distillate. Further, if each still is equipped with an efficient bubble cap or other type of tower, a practice which is followed in modern refineries, a product containing hydrocarbon fractions of closely related boiling points will be obtained, and little or no rerunning of the different fractions will be necessary.

56. Distillation in Pipe Stills.—Distillation of paraffin-base crude oils in pipe stills is no different from the operating procedure followed in distilling any type of crude oil in such units, except that slightly different temperatures are necessary to obtain a particular product, as compared with the practice followed in distilling any other kinds of crude oil in this type of still. Because of the valuable lubricating-oil fractions contained in paraffin-base crudes, however, extreme care must be taken during the distillation process that these fractions are not decomposed.

The tendency in the refining of paraffin-base crude oils is toward the distillation of the oil in equipment comprising pipe stills, separators, bubble or other towers, and heat exchangers, and to remove various products as overhead distillates and leave cylinder-stock bottoms. Rather than to scrap existing equipment, however, many refiners are finding it more economical to combine pipe and shell stills in the same distillation unit. Thus, in some refineries, a 1,200-barrel shell still is charged with crude oil. Then the tube-still furnace is fired and the pump that feeds oil to the tubes is started. A rotary pump, direct-driven by an electric motor and capable of delivering about 700 gallons of oil per minute, is used. This pump, in reality, serves as a circulating pump, as it withdraws oil from

the bottom of the shell still, forces it at high speed through the pipe coils in the tube still and then returns the oil again to the shell still. The oil travels through the tubes at the rate of about 6 feet per second. About three hours' time is required to raise the temperature of the oil from atmosphere to 150°–160° F., at which temperature vapors first begin to distil off.

When the gravity of the distillate coming over in the receiving house is 64°–65° A. P. I., steam at a pressure of about 45 pounds per square inch is turned into the shell still, slowly at first, by a slight turn of the valve on a 2-inch steam line. The steam is admitted into the still through a perforated pipe running along its bottom and the amount introduced is increased gradually as distillation proceeds.

57. The tubes in the pipe still may be 3½ inches in diameter and 13½ feet long and they are usually arranged in banks of four each, one bank above the other. After traveling through the tubes the hot oil and vapors are led through a 6-inch line into the bottom of the shell still, which they enter at a few inches from the bottom. The line extends the entire length of the still, being pierced on the under side with rows of ⅜-inch holes. These holes furnish the only means of escape for the hot oil and vapors from the tube still. The vapors rise through the volume of oil in the shell still and are led through a 12-inch vapor line to a tower. This tower is composed of two well-insulated drums, 42 inches in diameter and 6 feet high, placed one above the other with an air-cooled separator section between them. Each of the drums contain three trays packed with hollow tile so arranged that there is plenty of open space between the trays.

The vapors from the still enter the bottom of the lower drum. Mechanically entrained oil drops out first, which, together with hydrocarbons of higher boiling point that condense out before the top of the upper drum is reached, is refluxed into the shell still. From the top of the tower, the light vapors pass into condenser sections placed in a water-cooled condenser box. From the condenser, the condensate and uncondensed gases go into a separator. This is a vertical tank-like affair, 3 feet

in diameter and 8 feet high. Here the gases, the distillate, and the water resulting from the condensation of the steam used, are separated. The water is drawn off continuously from the separator and goes into a drain; the gasoline is taken off near the middle of the separator and runs through the condensate line into the receiving house; and the uncondensed gases are led off from the top. Gauge glasses indicate the heights of the liquid levels in the separator. The lightest gasoline condensed that passes through the look box in the receiving house has a gravity of 88° to 90° A. P. I.

58. Pressure- and temperature-recording instruments in the receiving house give the stillman complete information as to temperatures and pressures at various points in the system at all times. One recording thermometer shows the temperature of the oil in the shell still; one indicating thermometer, the temperature at which the oil enters the tube still; another, the temperature at which it leaves. One pressure recorder shows the pressure in the still, which pressure is nearly atmospheric; another, the pressure of the oil behind the pump, which oil is being charged into the tubes of the furnace. This pump pressure generally ranges between 10 and 12 pounds. Should a marked rise in pressure be noted, it would indicate the clogging-up of the apparatus, in which case the operation of the distillation unit would be stopped at once. Otherwise, there might be a rupture caused by the building up of pressure and fire might result.

59. Only three products are separated from the crude in the operation of this combination shell- and tube-still distillation unit, namely, light gasoline, heavy naphtha, and kerosene. The gasoline has a gravity of about 64.5° A. P. I., an initial boiling point of 110° to 112° F., and an end point of 408° to 410° F. The heavy naphtha has a gravity of 52.2° to 52.4° A. P. I., an initial boiling point of 260° F., and an end point of 446° F. The kerosene cut has a gravity of 45.2° to 45.4° A. P. I., an initial boiling point of 374° F., and an end point of 576° F. No products from the distillation require rerun-

ning, since they can be made marketable by a slight chemical treatment.

After the kerosene cut has been removed, the temperature of the oil is about 440° to 450° F. When the stream gravity is 44° A. P. I., the burners in the tube-still furnace are turned off and the distillation is finished down to 43° gravity with steam alone introduced into the shell still as the source of heat. About 26 hours' time is required thus to run down 1,200 barrels of paraffin-base crude oil. Finally, the residual oil in the shell still is pumped into the conventional type of fire stills, reaching these stills at a temperature of 400° to 410° F. In these stills a combined fire-and-steam distillation is given the oil, gas oil and wax distillate being removed as overhead products, while the bottoms is reduced to steam-refined cylinder stock of either 600°, 635° or 650° F. fire test.

60. Cracking Distillation.—Cracking distillation must not be confused with the various pressure and other cracking processes that are in use in nearly all refineries. This method of distillation was followed extensively in the early days of the industry, when burning-oil was the product most in demand, and gasoline was of almost no value. The growth of the automotive industry, however, has developed a rapidly growing market for gasoline and lubricating oils, so that new and improved methods for increasing the gasoline yield have come into use, while the lubricating-oil fraction has become much more valuable as such than as a material to be distilled destructively to increase the yield of lighter oils.

The cracking distillation is carried out by reducing the rate of distillation when the temperature of the oil in the still is from 600° to 650° F., and then heating the oil very slowly in the presence of little or no steam until the temperature of the still has increased 50° to 100° F. This process causes a decomposition or cracking of the oil, as a result of which, the yield of crude naphtha and kerosene distillate is increased. Very frequently, the residual oil resulting from the distillation of the crude in this manner, is distilled to coke in so-called coke or tar stills.

During the entire process of distillation, the gravity of the stream when it is transferred from one run-down tank to another (an operation that is necessary in order to separate products of different characteristics, such as naphtha, kerosene distillate, and gas oil), is approximately the same as when similar cuts are made during the fire-and-steam distillation of the crude oil.

TABLE I
COMPARISON OF YIELDS

Products	Fire-and-Steam Distillation Per Cent.	Cracking Distillation Per Cent.
Gasoline, naphtha, and burning-oils...	60.0	68.0
Gas oil and spindle oils.....	18.1	17.0
Unrefined wax	2.4	1.3
200-viscosity neutral oil.....	4.5	3.0
300-viscosity neutral oil.....		3.7
Cylinder stock and loss.....	15.0	
Coke and loss.....		7.0
Totals	100.0	100.0

A comparison of the yields of main products from the same paraffin-base crude by the two different methods of distillation is given in Table I.

DISTILLATION OF MIXED-BASE CRUDE OILS

61. Continuous Distillation in Shell Stills.—A detailed description of the operating procedures followed in the refining of mixed-base crude oils is difficult, as crudes of this type differ so widely in their characteristics and each refiner has developed methods that he believes to be the most economical and suitable. A brief description, however, is here given of the general process of operation followed by some refiners on a given crude. The equipment consists of a continuous battery of five shell stills, each of 600 barrels capacity; and during a 24-hour period 5,000 barrels of mixed-base crude oil, having an initial gravity of 36.5° A. P. I., are distilled.

TABLE II
SUMMARY REPORT OF CRUDE STILL RUNNING ON MIXED-BASE CRUDE OIL.

Time	Still No. 1		Still No. 2		Still No. 3		Still No. 4		Still No. 5	
	Gravity*	Temperature Still	Gravity	Temperature Still	Gravity	Temperature Still	Gravity	Temperature Still	Gravity	Temperature Still
7 A. M.	65.8	355	53.7	460	42.7	505	36.2	575	33.5	620
8	65.0	360	53.5	455	42.4	505	36.0	575	33.4	625
9	65.2	355	53.7	450	42.2	500	35.8	575	33.2	625
10	65.5	350	54.0	450	42.0	505	35.8	575	33.0	625
11	65.7	350	54.5	445	42.4	505	36.0	570	32.9	625
12 M.	65.8	355	54.8	450	42.4	500	36.3	570	32.7	625
1 P. M.	65.3	360	54.7	455	43.0	500	36.0	575	33.0	625
2	65.6	360	54.5	460	42.8	500	35.9	580	33.3	630
3	66.4	360	54.6	460	42.5	505	35.6	585	32.6	635
4	66.1	355	54.4	455	42.2	505	36.4	585	32.8	630
5	66.7	355	54.7	455	42.8	500	36.6	585	32.4	630
6	66.1	360	55.1	455	42.9	500	36.1	585	32.9	635
7	66.2	360	55.6	455	42.9	505	36.3	580	32.9	635
8	66.1	360	55.4	460	43.1	505	36.0	585	32.7	635
9	65.6	360	55.1	460	43.3	505	36.2	580	32.6	630
10	65.1	360	55.4	460	43.2	505	36.6	580	32.8	635
11	65.1	355	55.1	445	42.7	505	36.0	575	32.8	635
12 M.	67.2	310	55.6	435	43.2	500	36.0	575	32.2	635
1 A. M.	69.0	280	56.2	395	44.0	475	36.2	560	31.8	640
2	68.0	320	56.0	395	44.0	460	36.4	560	32.1	630
3	67.2	335	56.3	415	43.8	470	36.6	560	32.6	630
4	67.0	340	56.0	415	43.7	470	36.5	570	32.9	630
5	66.7	330	55.6	430	43.6	480	36.6	565	33.3	630
6	66.2	340	55.0	435	43.6	480	36.5	575	33.5	635

* All gravities shown in Table II are in A. P. I. degrees, and all temperatures are in degrees Fahrenheit

Table II shows the gravity of the stream from each still and the still temperature over a 24-hour period of time. The first two stills are equipped with fractionating towers, but there are no towers on any of the other stills.

Approximately one-half of the total gasoline yield from the crude oil is that which is obtained from the first still of the battery, and this subsequently is made marketable by a chemical treatment.

The crude naphtha or benzine from the second still is rerun either in steam stills or in combination fire-and-steam stills and a cut is made for gasoline, the fraction being collected from the beginning of the distillation until the gravity of the stream runs down to as low as 44.5° A. P. I. The gravity, of course depends on the end point that is desired on the total gasoline fraction. From the run-down tanks the gasoline is pumped to the agitators, treated, and then transferred to the proper storage tank. The residual oil resulting from the distillation of the benzine cut is pumped to storage, and when a sufficient quantity is available it is rerun in the fire stills, where the proper cuts are made for benzine and kerosene distillate, and the bottoms from this distillation is then pumped either to gas oil or to fuel oil, depending on the conditions that exist at the refinery.

62. Kerosene distillate is the product obtained from the third still of the battery. This is rerun either in steam stills or in fire-and-steam stills, making a cut for heavy gasoline down to about 44.5° to 45.0° stream gravity. The heavy gasoline, or "490 distillate," as it is also called, because it has an end point of approximately 490° F., will represent from 10 to 25 per cent. of the kerosene-distillate cut, depending upon the closeness of the fractionation on the continuous battery. Whenever it is practical to do so, some of this 490 distillate is blended with gasoline of low end point in order to raise the end point of the lighter product. Such a procedure serves to increase the total gasoline yield from the crude oil. Frequently, the heavy-gasoline cut is again rerun for a product of lower end point, in which case a gasoline cut is made down to about 44.8°

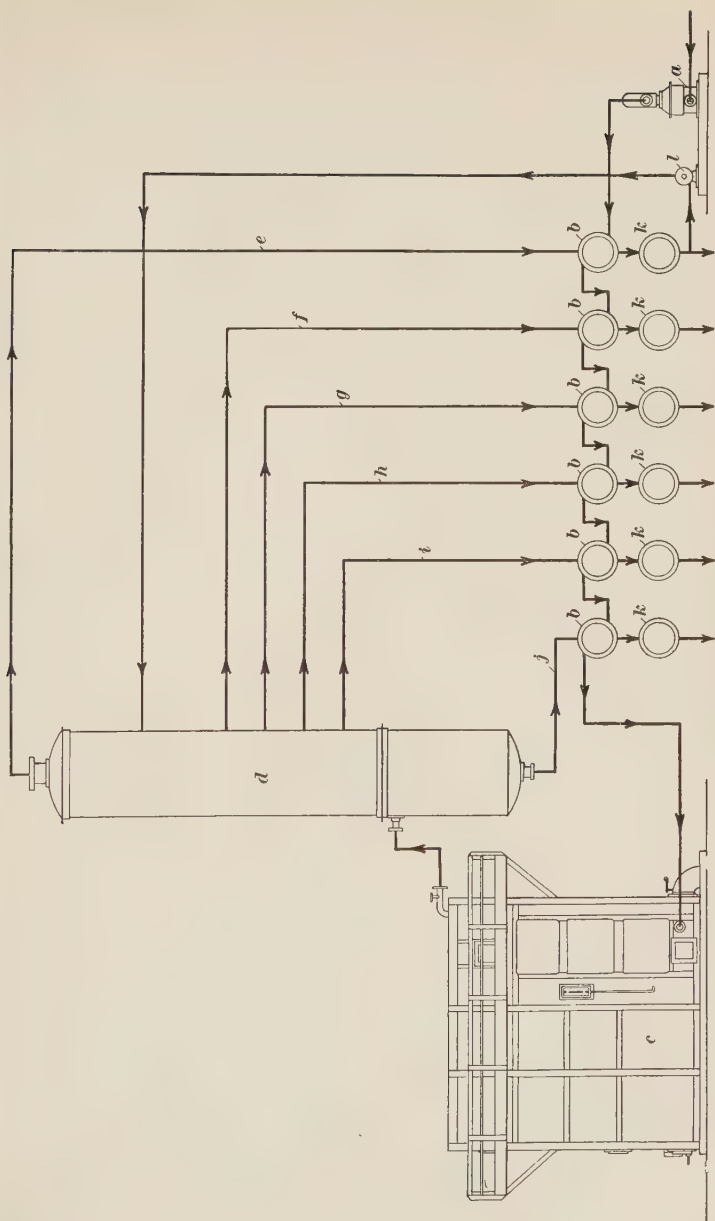
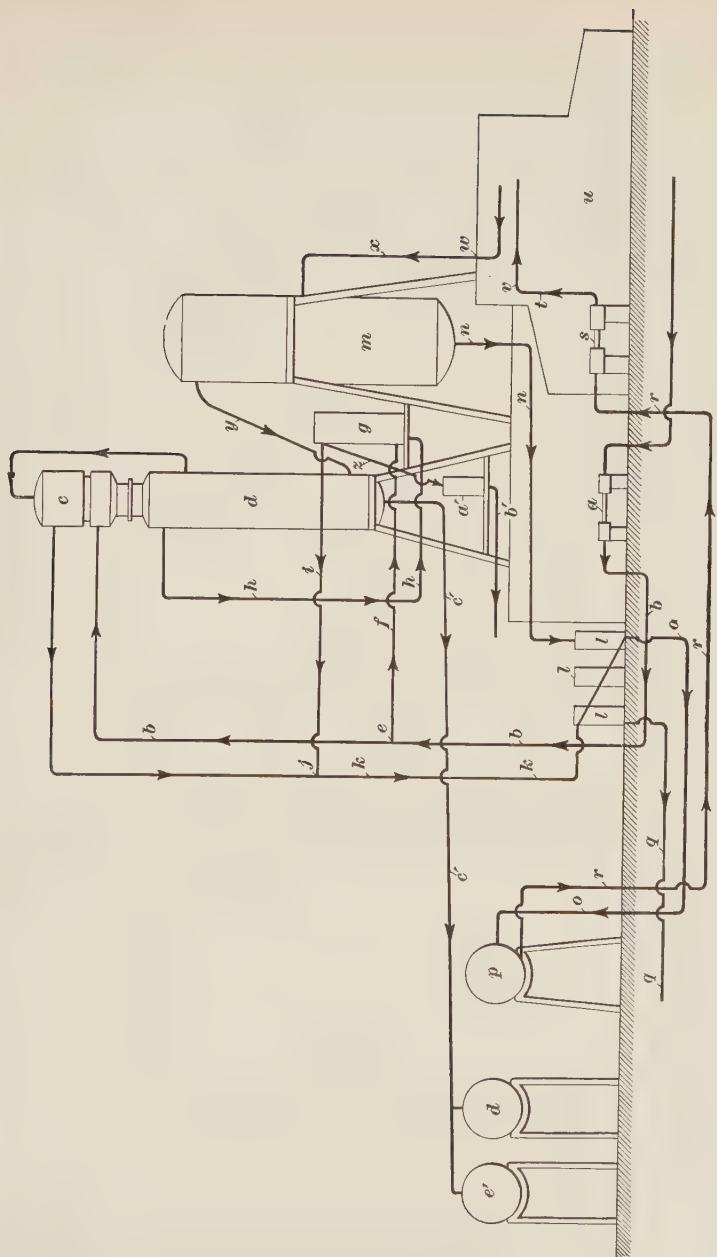


FIG. 5

stream gravity, and from that point until the stream goes off color into kerosene, the bottoms being pumped to gas-oil storage.

In rerunning the kerosene-distillate fraction, a cut for kerosene is made from 44.5° to about 37.5° stream gravity, or to the lowest gravity at which the color of the stream is good. The kerosene is then chemically treated in the agitators. The bottoms from the distillation of the kerosene-distillate cut is pumped to the gas-oil storage tank. The fourth and fifth streams of the continuous battery pass into the gas-oil tank and form the charging stock for the high-pressure stills. The average gravity of this cut is 34.5° A. P. I. The crude bottoms, as pumped from the fifth still, has a gravity of about 23.5° A. P. I. It is sold as such for fuel oil.

63. Distillation in Pipe Stills.—The variations in pipe-still design and operation among refiners, in processing any type of crude oil, are numerous. A diagrammatic sketch which indicates the construction and operation of a modern pipe-still distillation unit is shown in Fig. 5. As shown, the crude oil is forced by the pump *a* through the several heat exchangers *b* and into the pipe still *c*. From the pipe still, the vapors are discharged directly into a fractionating tower *d*. From this tower, are removed at different levels as overhead products, five different distillates, namely, gasoline, kerosene, gas oil, paraffin or wax distillate, and a high-viscosity lubricating stock, as indicated, respectively, by the lines *e*, *f*, *g*, *h*, *i*, and each of these distillates meets the required specifications as to initial boiling point and end point, and, with the heavier products, the flash point. A residual oil of any desired specifications is drawn off from the bottom of the tower. All of these products pass through the heat exchangers, give up most of their heat to the incoming crude oil, and then pass through the coolers *k* to their respective receiving tanks. Gasoline distillate is pumped back by the pump *l* over the top of the tower, as reflux, thus serving to aid in the fractionation of the products. Efficient heat exchangers conserve heat at all points and greatly reduce fuel consumption.



64. Another method of making use of a pipe still in a distillation unit is illustrated by Fig. 6. The main portion of the crude oil from storage, which has a gravity ranging from 39° to 40° A. P. I., is forced first by the pump *a* through the line *b* through the hot control section *c* of the fractionating tower *d*. Part of it may also be by-passed at the point *e* through the line *f* to the vapor heat exchangers *g* which receive their heat from the vapors that leave the fractionating tower through the line *h*. After coming from the vapor heat exchangers, the crude oil passes through the line *i* and joins the main stream at *j* which comes from the control section of the tower. It then passes through the line *k* to the heat exchangers *l* which are arranged in series. In these exchangers the oil is heated to a temperature of approximately 300° to 350° F., by the outgoing fuel oil brought from the expansion chamber *m*, through the line *n*. The crude oil then flows through the line *o* to the evaporator *p* which it enters at about the middle point. The heating oil from the exchangers passes to fuel-oil storage through the line *q*. In the evaporator, the lighter constituents of the oil vaporize because of its self-contained heat and the reduction in pressure. These vapors are led directly to a water-cooled condenser not shown. About 15 per cent. of the crude oil is thus distilled and obtained as a light-gasoline fraction.

From the evaporator, the topped crude oil is drawn through the line *r* by a hot-oil pump *s* and charged through the line *t* to the pipe still *u* at the point *v*. This still consists of 120 tubes, 3 inches in outside diameter, $\frac{1}{4}$ inch thick and 35 feet long, set in a combustion furnace. Provision is made for recirculating part of the flue gases and also for preheating the air required for combustion, as a result, fuel consumption is lessened.

The crude oil is brought to a temperature of about 750° F., before being discharged at the point *w* through the line *x* into the expansion chamber. The latter is 10 feet in diameter and 22 feet in height. All but about 15 to 20 per cent. of the crude oil is evaporated.

The vapors from the expansion chamber pass through the line *y* to the fractionating tower which is operated in such a

manner as to permit only the vapors of the gasoline that still remain in the oil, to pass to the vapor heat exchangers and finally through the line *s* to the condensers, one of which is shown at *a'*. From the condensers, the gasoline flows through the line *b'* to the tail house. The reflux oil that is drawn off from the bottom of the fractionating tower, is led by gravity, through the line *c'* to one of the two shell stills *d'* and *e'*. As this reflux oil, which represents about 40 per cent. of the original crude oil charged, accumulates in the shell still, the latter is fired and the lighter fractions are removed by a combined fire-and-steam, semicontinuous distillation, leaving gas oil as the residual product. Naphtha, kerosene, and furnace-distillate of various grades are the resultant products of the distillation of this 40-per cent. portion of the crude oil.

65. The foregoing description illustrates additional principles involved in pipe still distillation practice. The trend in the design and operation of distillation equipment is to preheat the crude oil in heat exchangers, then release the heated oil into evaporators and vaporize a portion of it, heat the remaining oil in a pipe still, and efficiently fractionate the resultant vapors. Many refiners also find it economical to draw off the residual oil from the bottom of the separator into so-called flash chambers, where the heat contained in the oil partly distills it, yielding a gas-oil cut as an overhead product. Likewise, where advisable, any intermediate fractions of the crude oil can be drawn off into flash chambers, partly distilled therein and the resultant vapors condensed, and a heat economy thus effected.

66. Cracking Distillation of Mixed-Base Crude Oils.—The cracking distillation of mixed-base crude oils, as in the case of paraffin-base crudes, is a process that is seldom used at the present time. Exceptions to this are those crude oils found in Mexico that contain both asphalt and paraffin, but little gasoline except that which is obtained as the result of a cracking distillation of the crude. However, the process as a whole is so rapidly passing out of use that it is necessary only to state that it involves the distillation of the crude to coke, using direct fire almost entirely as the source of heat. As a result of such

distillation, the yield of lighter distillates is increased, but the lubricating oils obtained are apt to be of inferior quality as compared to those resulting from the fire-and-steam distillation of the crude. Furthermore, fuel oil is more in demand than petroleum coke, particularly since coke is a by-product of the various patented cracking processes, which are installed in nearly all refineries for making gasoline out of gas oil or fuel oil.

CHEMICAL TREATMENT AND PURIFICATION OF LIGHT OILS

67. Impurities in Light Oils.—The light distillates obtained from the distillation of crude oil or from the cracking of heavy oils in most cases are not marketable until after they have been purified. Almost all crude oils contain certain impurities, the most objectionable of which is sulphur. This impurity is sometimes present to a slight extent in gasoline and kerosene as free sulphur, but to a greater extent in the form of complex chemical compounds. These sulphur compounds must be removed, otherwise, the gasoline will corrode certain parts of the gasoline engine in which it may be used, and the kerosene will not burn properly in a lamp or stove. Oils are purified, that is, treated, either by physical or chemical means, or by a combination of the two. Treatment also improves the odor and color of an oil and, in general, makes the product fit for use. The nature of the chemical treatment given any light oil depends primarily, however, on the characteristics of the product being handled and the degree of refinement desired. In most cases it is advantageous to determine first in an experimental way the particular treatment to be given each different kind of product, especially when the crude oil from which it is obtained varies from time to time.

68. Batch and Continuous Treatment.—Light oils may be treated by either the batch, the continuous, or the batch-circulating method, each of which requires different equipment.

Batch treatment is conducted in an upright, conical-bottom tank, known as an agitator. Such agitators vary in size from 200 to 5,000 barrels, depending on the size of the refinery. The tank, or agitator, is properly supported and is fitted with piping

for charging and pumping out the oil, for drawing off both the reaction products, or sludge, and the water used in washing, as well as with piping for blowing with air. It is also equipped with piping, pumps and other accessories necessary for the preparation and addition of chemicals, and the piping and spray arrangement needed for washing the oil with water.

Systems for treating light oils continuously are in use in most refineries, because in most cases their use is more economical than batch treatment. A type of continuous treating plant for light oils that is used extensively in this country, consists of a series of closed vertical tanks, into the first of which the oil is steadily pumped, admixed with sulphuric acid and then allowed to settle. It is next pumped to a second tank, washed with water, which is permitted to settle out, and the oil is then treated with either a caustic-soda or sodium-plumbite solution in a third tank. The chemicals are then allowed to settle out and the oil is further washed with water. All of the foregoing is done in a continuous operation in succeeding tanks. The total number of these tanks may range from six to ten, depending on the condition of the oil. A lesser number of tanks may be used, however, when treatment with acid is not necessary and the oil requires merely admixture with a sodium-plumbite solution.

69. Construction and Operation of Batch Circulating Plant.—A typical batch circulating plant for treating oil is shown in Fig. 7. It consists of a mechanical mixer made up of three lengths *a*, *b*, and *c*, of 24-inch standard pipe, each of which is 8 feet long and fitted with heads and stuffingboxes on the ends, the whole resting in a horizontal position in a steel cradle *d*. Each cylinder is equipped with a shaft to which are attached four 4-bladed propellers *f*, built somewhat similar to the ordinary electric fan. The propellers are so mounted that the throw of the second is opposed to the first; and the throw of the fourth, to the third, in order to provide maximum agitation and contact of the oil and chemicals. The shafts between each unit are connected with flexible couplings to permit of one common power application. In addition, the three cylinders are con-

nected to each other on the side by a pipe 8 inches in diameter. This permits a continuous flow of the liquid through the apparatus. The mixer is run at a speed of 100 to 150 revolutions per minute.

In the operation of the system, the gasoline or other distillate to be treated is forced by the pump *j* into the first mixing unit and compressed air is introduced from the tank *g*. After circulating through the mixing cylinders, the mixture of gasoline, chemicals and air is run from the end of the third unit into

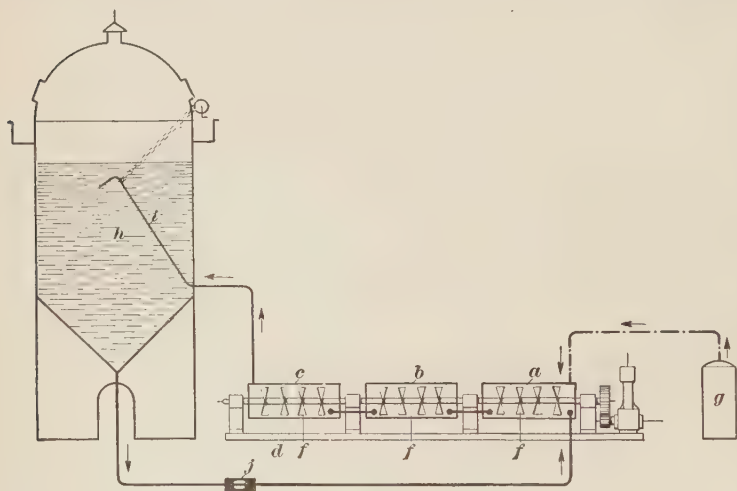


FIG. 7

a batch agitator *h*, which it enters through a line *i* near the top. In the agitator the air escapes. The chemicals and gasoline are then pumped from the bottom of the agitator by the pump *j* and continuously recirculated through the cylinders, new air being added until the reaction between the sodium-plumbite solution and the sulphur compounds contained in the oil is satisfactory. A small amount of free sulphur is then introduced, and the circulation is continued until the reaction has been completed. The gasoline is then given a thorough spray-washing with water. Gasoline thus treated with sodium-plumbite solution (the so-called doctor solution) and sulphur, is said to have been sweetened.

70. Sodium-Plumbite Treatment.—Ordinarily, the sodium-plumbite, or doctor, treatment, is all that the gasoline requires. The doctor solution is prepared by mixing litharge with a strong solution of caustic soda. Litharge is soluble in a 15° Bé. caustic-soda solution to the extent of 2 per cent., which solubility is increased to only 2.75 per cent. in a 30° Bé. caustic solution. Doctor solution as generally used has a gravity of 15° to 20° Bé. This solution loses strength in use; consequently, when it reaches about 8° to 10° Bé., it is either replaced with a new solution, is restrengthened, or is used for a different purpose. The doctor treatment, or sweetening, of an oil in a batch agitator consists merely in air-agitating the oil with sodium-plumbite solution, such a quantity of the latter being used as is necessary to cause the sodium plumbite to react with the active organic sulphur compounds contained in the oil in order to sweeten it quickly. After agitating for a sufficient length of time, a small amount of flowers of sulphur is generally added and the agitation is continued. Best results are obtained if the amount of sulphur to be added is first determined experimentally in the laboratory, especially since a few pounds extra of sulphur in a 1,000-barrel batch will often cause the gasoline to fail to meet the corrosion test. The excess sodium-plumbite solution and the products of the reaction are allowed to settle to the bottom of the agitator, blowing with air meanwhile having been stopped, and are then drawn off. After washing by agitation with water, settling, and drawing off the water, the gasoline is pumped to a storage tank and is ready to be marketed.

71. The chemical principles involved in the sodium-plumbite treatment, are essentially as follows: If hydrogen sulphide is present in appreciable quantities in the oil undergoing treatment, a black precipitate forms immediately when the sodium-plumbite solution is added to the oil. When a considerable amount of hydrogen sulphide or organic compounds of sulphur is contained in the oil, refiners usually find it advantageous to give the oil a preliminary wash with a caustic-soda solution before introducing the doctor solution. This pre-

liminary treatment saves the lead in the doctor solution which, otherwise, would be precipitated as lead sulphide. In doctor treating, the precipitate that first forms is usually of a yellow or an orange color, and on standing, changes to brown and finally to black. In some cases the treatment with sodium-plumbite solution merely imparts a yellow color to the oil, but no precipitate is formed until after a small quantity of sulphur has been added. The latter operation is known as breaking-out, and, on the formation of the precipitate, the oil is said to have "broke." When no hydrogen sulphide or free sulphur is contained in the oil, the sodium plumbite and the organic sulphur compounds, or mercaptans, combine to form lead mercaptides and caustic soda. Then when free sulphur is added, organic disulphides and lead sulphide are formed. The disulphides are soluble in the oil, but the lead sulphide is precipitated. The gasoline or other product treated in this manner has a good odor, is sweet, and will give a negative reaction to the doctor test.

72. A method of treating light oils that has received considerable attention, involves the use of lead sulphide or so-called spent doctor solution.

In a current of air, lead sulphide in suspension in a caustic-soda solution is slowly oxidized to lead sulphite, then to the thiosulphate and finally to the sulphate form. These compounds are soluble in the caustic-soda solution, sodium plumbite and sodium sulphate being formed. Thus, in the presence of oxygen, as when an oil is blown with air, lead sulphide will sweeten even those gasolines that ordinarily are extremely difficult to treat. It is also widely believed that, in this sweetening process, the lead sulphide apparently has a catalytic effect in speeding up the action of the doctor solution, and, in addition, adsorbs and holds mechanically to it large quantities of mercaptans, thereby making it less difficult for the sodium-plumbite reaction to be completed.

To guard against the contamination of a distillate that is undergoing the sweetening process, it is necessary that the apparatus be absolutely clean and free from lead sulphide, sul-

phur and other sludging materials resulting from previous treatments. Also, the accumulation of sulphur-bearing scale and sludge in the run-down tanks should not be permitted since, if such deposits are not removed at regular intervals, the gasoline will tend to redissolve so much sulphur that the treatment cannot be easily regulated to produce a finished oil that will pass corrosion tests.

73. Recovery of Spent Doctor Solution.—In many cases refiners find it economical to recover the spent doctor solution. In one method of reclamation, the spent doctor solution, which contains lead sulphide suspended in caustic-soda solution, is drawn from the agitator into a tank equipped with closed steam and perforated air coils. Compressed air passes through perforations in the air coils at the bottom of the tank, agitates the lead sulphide and oxidizes it, first, to lead sulphite, then, to lead thiosulphate and finally to lead sulphate. On the completion of the reaction, the originally black solution will have cleared up until it is either colorless or of only a slightly reddish color. The temperature is controlled by the use of the closed steam coils. During the oxidizing process, a maximum temperature of 200° F., is reached. The effect of the heat is to help the oxidation and to decompose objectionable sulphur compounds and other impurities that are usually present in spent doctor solution. The latter is now called reclaimed doctor solution and, as such, is stored until used. The properties of this solution are very similar to and have the same effect on gasoline as new doctor solution.

74. Acid and Alkali Treatment of Straight-Run Distillates. Frequently in the treatment of kerosene, and particularly so in the treatment of distillates from pressure stills, a more vigorous chemical treatment than the one just described is necessary in order to make the product marketable. In the batch agitator, the oil is usually treated with from 1 to 8 pounds of 66° Bé. sulphuric acid for each barrel of oil, acid in the higher amounts being used in treating kerosenes and more refractory distillates. If more than 1 pound of acid to the barrel of distillate is used, it is added, usually, in two portions. The first portion, or dump,

of acid may vary from $\frac{1}{4}$ to 1 pound for a barrel. This is called the water-acid dump, since it is used principally to free the oil of moisture before the remainder of the acid is introduced. If there is excessive moisture in the oil, when a relatively large quantity of acid is added at one time the reaction between the acid and water will so increase the temperature of the oil that there will be a tendency to burn the oil, thus darkening it instead of improving its color. After each addition of acid, the oil and the acid are agitated with air for the shortest time required to obtain the desired results; this time may vary from a few minutes to over an hour. Agitating the distillate with too much air or for too long a time causes an excessive oil loss. After agitation has been stopped, the oil is allowed to remain undisturbed until the sludge has settled. The sludge is then drained from the agitator, and the oil is washed thoroughly with water by means of sprays placed above its surface. A weak solution of caustic soda of about 6° to 12° Bé., is then pumped into the agitator, and the oil is again agitated with air, after which the caustic-soda solution is allowed to settle and is drawn off from the agitator. The treatment is completed by a second spraying with water. Washing with water is continued until there is no indication of caustic soda in the treated oil. The treated product is then pumped from the agitators to storage tanks.

75. Kerosene is usually treated with sulphuric acid and caustic soda in a light-oil batch agitator in a manner similar to that just described. The principal points of difference are that more acid is required, the time of agitation is longer, and much more water is used for washing purposes. When the desired color is not obtained and the lamp burning test is not satisfactory following such a chemical treatment, it is a frequent practice either to treat the oil in the agitator with fullers' earth or to percolate the treated kerosene through a column of coarse fullers' earth. Such a physical treatment with fullers' earth improves both the quality and the marketability of the kerosene, since objectionable impurities are thus adsorbed by the clay.

An outline of a typical chemical treatment for blending naphtha, is shown in Table III. It must be emphasized, however, that it is almost impossible to give typical methods of treating oils, since, the variations are so many. These variations are largely dependent on the chemical composition of the oil being treated.

TABLE III
CHEMICAL TREATMENT FOR BLENDING NAPHTHA

Operation	Time
Charging 1,000 barrels of oil to agitator.....	3 hours
Settling until test on product in agitator is obtained from laboratory.	
Addition of 4 pounds of acid per barrel of oil.	
Air blowing of acid and oil.....	20 minutes
Settling	30 minutes
Drawing off sludge from bottom of agitator.	
Second addition of 4 pounds of acid per barrel of oil.	
Air blowing of acid and oil.....	20 minutes
Settling	1 hour
Drawing off sludge.....	
Spray-washing oil with cold water.....	45 minutes
Settling	1 hour
Drawing off water.	
Addition of 1 pound of 20° Bé. caustic-soda solution per barrel of oil.	
Settling	1½ hours
Drawing off excess soda solution.	
Pumping naphtha to storage.....	3 hours

Many refiners use doctor solution instead of caustic-soda solution following the treatment of the oil with sulphuric acid.

76. A typical method for chemically treating kerosene is outlined in Table IV. It is often found advantageous to give the oil a preliminary treatment with a weak caustic-soda solution.

77. Chemical Treatment of Cracked Distillates.—Cracked distillates, or pressure distillates, which have already been

described briefly, contain not only gasoline but also oils of lower gravity. These distillates are subjected to a variety of chemical treatments, three of the most important of which are as follows:

TABLE IV
CHEMICAL TREATMENT OF KEROSENE

Operation	Time
Charging 1,000 barrels of oil to agitator.....	3 hours
Settling	2 hours
Addition of 0.1 pound of 8° Bé. caustic-soda solution per barrel of oil.	
Air blowing of caustic soda and oil.....	10 minutes
Settling	30 minutes
Drawing off excess caustic-soda solution.	
Spray-washing oil with water.....	30 minutes
Settling	1 hour
Drawing off excess water.	
Addition of 3 pounds of acid per barrel of oil.	
Air blowing of acid and oil.....	20 minutes
Settling	30 minutes
Drawing off sludge.	
Second addition of 5 pounds of acid per barrel of oil.	
Air blowing of acid and oil.....	20 minutes
Settling	30 minutes
Drawing off sludge.	
If color of oil is not as desired, additional quantities of acid may have to be added.	
Spray washing of oil with cold water.....	1½ hours
Settling	1 hour
Drawing off excess water.	
Addition of 1¼ pounds of 20° Bé. caustic solution per barrel of oil.	
Air blowing of oil and caustic solution.....	1½ hours
Settling	1 hour
Drawing off soda solution.	
Pumping kerosene from agitator to bleachers for removal of all moisture.	

Method No. 1.—This method, which is applicable to the types of cracked distillates that are treated with least difficulty, con-

sists in agitating the oil with 66° Bé. sulphuric acid, allowing the sludge to settle, drawing it off, and washing the oil with water. After the water has settled out, it is drawn off and the oil is treated with sodium-hydroxide solution. The solution is then allowed to separate, is drawn off and the oil is again washed until free from alkali, each portion of wash water being allowed to settle and then being drawn off. The chemically treated oil is then steam distilled, the process being assisted in some cases by means of a low fire under the still. Preferably the distillation should be of the semicontinuous or continuous type in order to avoid long-continued heating of the oil.

Method No. 2.—This is the most desirable and most generally applied method for the treatment of cracked distillates. It is practically the same as Method No. 1, except that a sodium-plumbite treatment replaces the sodium-hydroxide treatment. In the description of the method, reference to such operations as settling of wash water and sludge, and the drawing off of these by-products, will be omitted.

The distillate is agitated first with 66° Bé. sulphuric acid, and washed with water for 5 to 10 minutes. It is then agitated with sodium-plumbite solution and should, at this stage, show a negative doctor test. Whether or not a precipitate is formed on the addition of the sodium-plumbite solution, the latter is allowed to settle and is drawn off. Sulphur is not added. The distillate is then redistilled with steam, aided by a low fire under the still. If the gasoline distillate obtained gives a positive doctor test or is sour, it should be sweetened by treatment with sodium-hydroxide solution, using the weakest solution that will accomplish the desired result.

It is sometimes desirable to precede the acid treatment by a water wash to remove undesirable water-soluble compounds such as hydrogen sulphide. A caustic-soda wash followed by a water wash serves the same purpose to a greater degree.

Method No. 3.—This method is applicable especially to cracked distillates from light or heavy California, Mexican, South American, and similar oils, and gives a sweet, stable product seldom obtainable, by the methods previously described, with cracked distillates from these types of oils. The method

is known as the split plumbite method, because the plumbite treatment both precedes and follows the acid treatment.

The water wash is applied first and the oil is then treated with sodium-plumbite solution, preferably of greater gravity than 20° Bé. After the washing, sulphuric acid is added in the proportion of about 1 pound for each barrel of distillate. The mixture is then agitated and the sludge drawn off. The remainder of the sulphuric acid is then added if laboratory tests show that a further addition is necessary. When the sludge has again been removed, the oil is agitated with sodium-plumbite solution having a gravity of approximately 10° to 16° Bé. The latter is then removed and the treated distillate is distilled with steam. If the gasoline distillate comes over sour, it is treated with the most dilute solution of sodium hydroxide that will sweeten it. However, if laboratory tests show that the distillate cannot be sweetened in this manner, the use of a dilute solution of sodium plumbite will accomplish the desired result.

78. Continuous Treating Systems.—All the operations mentioned in the three methods of chemical treatment just described, may be applied to either batch or continuous treatment of cracked distillates. Continuous treating systems using orifice columns, packed columns, baffled coils, or other mixing devices, are economical from the viewpoint of through-put and cutting down of losses by evaporation.

The orifice column, which is a satisfactory mixing device, consists of short lengths of flanged pipe, between the flanged joints of which are inserted the orifice plates. Ordinarily, these are steel plates, or disks, with perforations which in succeeding plates do not coincide. Therefore, as the distillate and reagent are pumped through the columns, the mixture is caused to change its direction of flow many times, thus causing efficient mixing. Mechanical mixing or circulating devices such as centrifugal, gear, or other type pumps, when applied to batch agitators instead of air-blowing, also cut down evaporation losses.

Continuous treating systems ordinarily consist of combinations of mixing, settling, and washing arrangements, depending on the method of treatment. The mixing arrangements usually

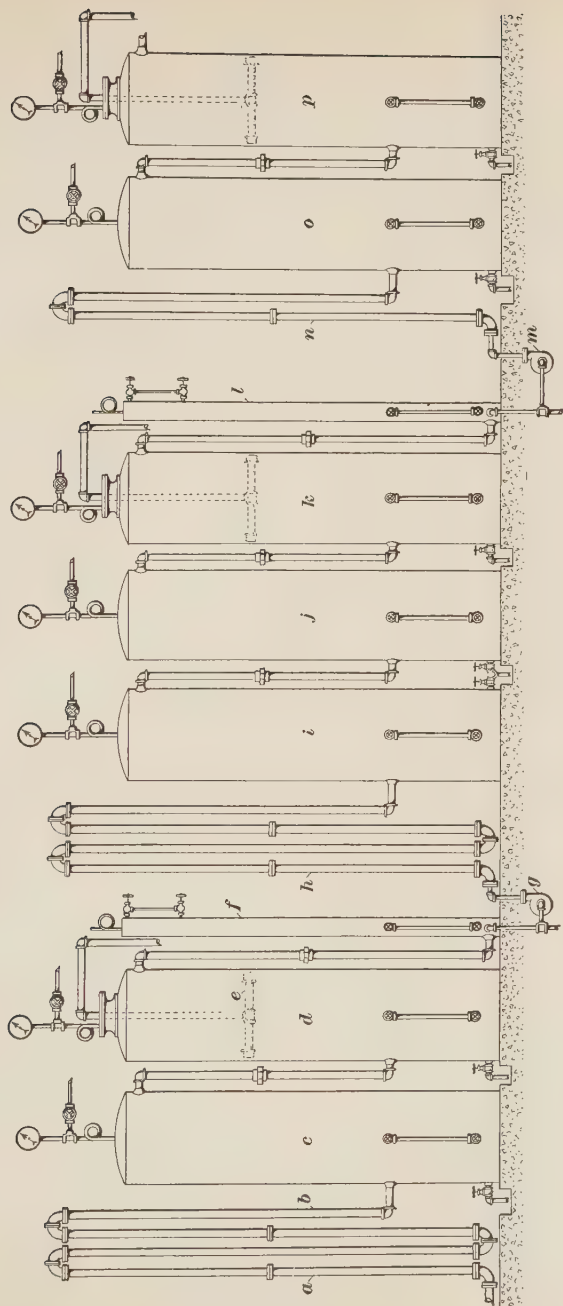


FIG. 8

consist of orifice or baffled columns or coils that discharge into a settling chamber from which the oil overflows into another settling chamber when necessary, and under any circumstances into a washing chamber equipped with a spray washer placed below the overflow level. Before the oil is subjected to the action of the next reagent or mixing stage, it is good practice to discharge it into a reservoir or surge tank which permits regulation of the flow of oil and proper proportioning with regard to the succeeding reagent, which may be sodium-plumbite solution or sodium-hydroxide solution.

A continuous treating arrangement suitable for any type of treating and especially for the split plumbite method, is shown in Fig. 8. It consists of a sodium-plumbite mixing column or coil *a*, equipped with orifice mixers at *b*, a sodium-plumbite settling chamber *c*, a water-wash chamber *d*, equipped with a spray *e*, a reservoir or surge tank *f*, a booster pump *g*, an acid mixer *h*, two acid settling chambers *i* and *j*, a lead-lined water-washing chamber *k*, a second reservoir or surge tank *l*, a booster pump *m*, a plumbite mixing column or coil *n* for the second plumbite treatment, and finally, a plumbite settling chamber *o* and a washing chamber *p*, which is also equipped with a water spray.

The reservoirs, or surge tanks, may be 10 or 12-inch columns, in proper serial arrangement and of the same height as the settling chambers, and equipped with sight or gauge glasses. The settling chambers are also equipped with gauge or sight-glasses and drains for drawing off sludge acid, waste alkali, or sodium-plumbite solution and wash water. The charging pump for the pressure distillate is equipped with a meter. The booster pumps may be likewise equipped. Drain and feed cocks should be of the self-lubricating type. Blow cases are installed in duplicate to permit periodic gauging. Acid and sodium-plumbite solution storage tanks should be provided. Manometers are useful for testing differential pressures at various points.

79. Low-Temperature Treatment of Cracked Distillates.

An improved method of treating cracked distillates involves the admixture of the oil and acid at reduced temperatures. By

this method, oil constituents of high antidetonating value are conserved, yields are increased, and treating costs are reduced to an extent that permits the refining of even the more refractory distillates, which cannot be treated profitably by other methods. This process is illustrated by the flow chart shown in Fig. 9.

The pressure distillate, which may be crude naphtha, is forced by the pump *a* into the tank *b*, where it receives a preliminary treatment with caustic soda, and after being washed and settled in the tanks *c* and *d*, is finally dried by contact with the spent acid in the drier *e*. Drying is necessary in order to remove water that otherwise would freeze in the cooling coils during the subsequent operation.

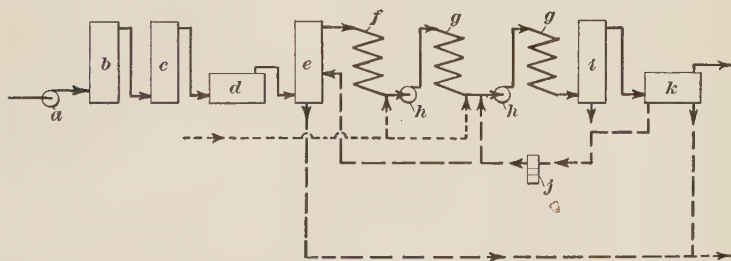


FIG. 9

After settling of the acid, the naphtha is cooled to a temperature of approximately 25° to 30° F. below the maximum temperature desired for the treatment, that is, to about 5° F. The cooling may be done in one or more stages and is carried out in specially designed coolers, that consist of coils that are surrounded by ammonia. The first of these coolers are termed precoolers to distinguish them from the reaction coolers *g*, which follow the spent-acid, or drying, treatment.

From the precoolers the naphtha passes to the acid mixers *h*, in which the acid is applied to the oil in two or more stages. For convenience, centrifugal pumps are used, both as mixers and boosters. The application of the acid in several stages permits of better temperature control and provides for the absorption of some of the heat of reaction in coolers after each mix-

ing pump. The distribution of acid between the mixers is such that the temperature is the same after each application, this temperature being the desired maximum. Each application of acid is followed by another cooling of naphtha and sludge in a reaction cooler. The mixed naphtha and sludge then pass to the sludge settlers *i* where the sludge is removed, the spent acid being returned to the drier by the pump *j*. The sludge that collects in the drier and settlers is sent to the sludge pans for the recovery of the acid that it contains. The treated naphtha then goes to the auxiliary settler *k* and finally to the water washers and caustic treaters for the neutralization process. The washing with water and the neutralization take place at ordinary temperatures. The treated distillate is then rerun by a combined fire-and-steam distillation.

80. Hypochlorite Treatment.—The hypochlorite treatment of oils is used most extensively in the purification of so-called natural-gas gasoline, which is gasoline obtained from gas wells and from the gas issuing from flowing oil wells, but it is used to some extent also in the treatment of high-gravity refinery gasolines. The equipment needed and the method of procedure is very similar to that followed in the ordinary treating of light oils with the exception, for the most part, that a solution of either sodium or calcium hypochlorite is used instead of the doctor solution. Since hypochlorites are oxidizing agents, they oxidize the sulphur compounds in the oil to other compounds that are free from odor and color. These oxidized substances are then removed from the oil undergoing treatment by subsequent contact with water and alkali in which they dissolve.

A typical treatment consists of an initial wash with an 8° Bé. caustic-soda solution, followed by a wash with water. Two separate washes with sodium-hypochlorite solution are then given and followed by a wash with caustic-soda solution and finally with water.

In all cases, the exact method of treatment and the quantity and strength of hypochlorite solution that will give best results will depend on the product being treated and the degree to which the refining is to be carried. For straight-run distillates

the strength of the hypochlorite solution can vary between 20 and 30 grams of available chlorine per liter. With cracked distillates better results are obtained in most cases by the use of weaker solutions that contain from 5 to 10 grams of chlorine per liter. The amount of hypochlorite to be used can be predetermined in the laboratory for any given distillate. This method of treatment can be applied either in batch agitators, or in batch circulating or continuous treating systems.

81. Edeleanu Process.—The Edeleanu process, which was originally developed in Europe, for producing non-smoking kerosene from crudes high in content of aromatic hydrocarbons, has been installed in several California refineries. The process is based on the fact that if the distillate to be treated is agitated with liquid sulphur dioxide at low temperatures, say from 8 to 10° F., the objectionable aromatic compounds contained in the oil are dissolved, and the paraffins and naphthenes are unaffected. In carrying out this method of treatment, addition of liquid sulphur dioxide is continued even after the distillate is saturated, as each portion of sulphur dioxide added thereafter helps to dissolve the aromatic constituents and separates out with them as a distinct layer. As treatment proceeds, the distillate becomes poorer and poorer in objectionable aromatic hydrocarbons, until eventually a refined distillate is obtained. This distillate contains only a small amount of sulphur dioxide and is almost entirely free from detrimental aromatic constituents. In order to obtain the best results, each distillate, depending on its composition, requires for treatment the use of different temperatures from that of any other distillate. This is due largely to the fact that paraffin and naphthene hydrocarbons are soluble in liquid sulphur dioxide at the higher temperatures but almost entirely insoluble at low temperatures, whereas the aromatic hydrocarbons are soluble in sulphur dioxide at all temperatures. Therefore, as the compositions of different oils vary, slight changes in treating temperatures become necessary. It is of the utmost importance for the success of this process, particularly in the treatment of distillates containing a relatively large percentage of aromatics, that the temperatures

be maintained at a suitably low level. The treatment is completed by washing and neutralizing the treated distillate with an alkaline solution, either in batch agitators or in a continuous treating system.

PHYSICAL METHODS OF TREATMENT

82. Contact Treatment in Liquid State.—By physical methods of treatment are meant those processes in which the impurities present in an oil are retained, mechanically, by an adsorbent medium, as compared with the methods in which a chemical reaction takes place between the purifying agent and the undesirable constituents contained in the oil undergoing treatment. Physical methods of purification may be applied when the oil is in either the liquid or the vapor state.

Finely divided fullers' earth, specially prepared acid-treated clays, and silica gel are used by refiners in purifying oils in a liquid state by the so-called contact method of treatment. In such instances, the material used is of 100- to 200-mesh in fineness. These adsorbent mediums may be used under a variety of conditions. Thus, the clay may be applied to the oil in place of a doctor treatment, or immediately following either a sodium plumbite or a combination acid and neutralization treatment; or, after an acid treatment alone, in which case the clay serves both to decolorize and to deacidify the oil.

In one method of carrying out the treatment, the amount of clay required may be mixed with a small portion of the oil to be treated, until a product of the consistency of thick cream is obtained. This mixture may then be brought into contact with a large quantity of the untreated oil, as in an agitator, or with a stream of oil, as in a continuous mixer or centrifugal pump. This method of application is especially suitable when clay is to be used instead of an acid treatment, and where continuous-treating apparatus is already available, because the clay can be fed into the stream of oil at the point where the acid ordinarily enters. Furthermore, in most cases, the same tanks or mixers used in the acid-treatment method may be employed for keeping the clay in contact with the oil during the time necessary for adsorption of the impurities to take place.

83. When oil is treated in a batch agitator, the required amount of clay can be introduced either directly into the oil from a bag or, preferably, through a continuous feeder or a small shaking screen. The oil should be kept well agitated during the introduction of the clay, which should not be added in a mass, that is, a full sack at one time, for such action will tend to cause the formation of balls of clay that are wet with oil on the outside but dry within, and such lumps are difficult to break up. Circulation through centrifugal pumps, by pumping oil out from a point near the top of the agitator and in again at the bottom, is preferable to agitation with air, since clay is much lighter than acid and does not require violent agitation in order to keep it in suspension.

Clay treatment tends to stabilize the color of gasolines from many types of crudes, particularly that from California. For this reason, clay treatment of gasoline first gained prominence in California. The amount of clay used in treating gasoline varies from $\frac{1}{8}$ pound to 2 pounds per barrel, the required quantity usually being determined first experimentally in the laboratory. Not all gasoline can be purified economically by the use of clay alone. For making dark-colored or otherwise refractory oils marketable, it is much more economical to give the oil a slight treatment with acid, and then use clay in place of the caustic soda and water wash. The clay should be applied to the cleanly settled oil in an agitator separate from that in which the oil was treated with acid. From 15 to 30 minutes ordinarily is a sufficient period for the oil and clay to be in contact with each other. Less time is necessary on acid oils than on those that have already been neutralized with an alkali.

To reduce oil losses to a minimum, filter presses are commonly used to separate the spent clay from the oil. In such presses the clay is retained on a separating medium, such as cotton or woolen blankets or Monel metal screens, while the clay-free oil passes on to storage. Separation of the clay in filter presses is a continuous operation, being interrupted only when the spaces between the cloths become filled with clay. Steam, air, or gas, is blown through the equipment to dry the clay, after which the press is opened and the clay removed.

84. Silica-Gel Process.—The silica-gel process is based upon the adsorbing properties of silica gel, which is a pure form of silica made by mixing in proper proportions, solutions of sodium silicate and sulphuric acid, washing the jelly-like mass thus formed and subsequently drying the material to the desired point. The oil to be treated is brought into contact with the gel by a continuous and counter-current method, during which operation objectionable impurities in the oil are adsorbed by the gel. Suitable furnaces are provided for reactivating the material so that it can be used over and over again.

85. Contact Treatment in Vapor State.—The Gray vapor-phase method of treating cracked-gasoline vapors before condensation is extensively used by refiners. By this method, the gasoline vapors as they come over from the still are passed through fullers' earth having a fineness of 30 to 60 mesh or 60 to 90 mesh; that is, earth that will either pass through a screen having 30 meshes to the linear inch and be retained on one having 60 meshes, or that will pass through a 60-mesh screen and be retained on one of 90 meshes.

The clay polymerizes some of the unstable, unsaturated hydrocarbons into more stable compounds of higher boiling point and removes most of the color compounds and other easily decomposed components of the gasoline. These polymers collect and are removed continuously from the clay. The process is equally applicable for use either in connection with pressure cracking stills or with fire-and-steam stills rerunning pressure distillate. The towers used are 8 to 12 feet in diameter and 16 to 18 feet in over-all height. The inner chamber, varying with towers of different sizes, will hold 8 to 20 tons of fullers' earth.

In Fig. 10 is shown how a Gray tower is connected with the bubble tower of a Cross cracking unit. Two towers are provided for alternate use with this unit, but only one is here shown.

The oil and vapors come into the vapor tower *a* in which the oil collects at the bottom and is drawn off, and the vapors go to the bubble tower *b*. Gasoline vapors are then taken off from

the top of the bubble tower to the desired end point. The vapors go direct to the polymerizer, or Gray tower *c*, and follow a circular path upward through the outer chamber *d*, then downward through the clay in the clay chamber *e* and out through the lower compartment *f* to the condenser *g* and the gas separator *h*. There is partial condensation of the vapors in the outer shell of the tower and these, which also constitute the reflux, are taken care of by means of an automatic stream regulator *i* on a draw-off line running to the pot *j*, a constant

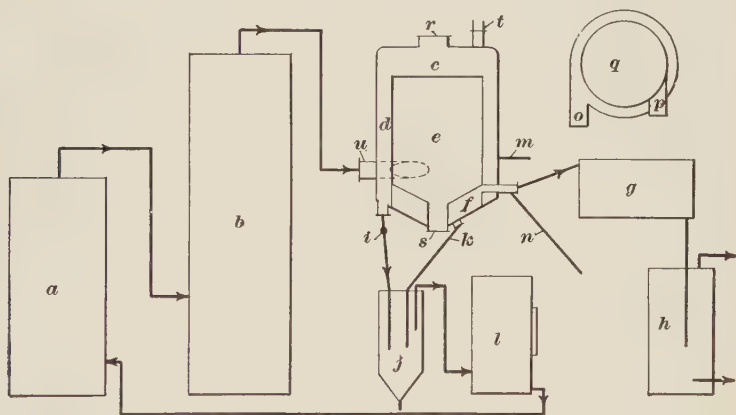


FIG. 10

level being maintained in the tower. The polymer line *k* opens directly into the pot, the polymers also being drawn off into the pot as they collect in the lower compartment *f*. Both the reflux and the polymers pass into the accumulator tank *l*. An electric pump connected to the outlet line on this tank operates intermittently to pump the reflux and polymer fractions to the bottom of the vapor tower *a*. The Gray tower is equipped with a 2-inch, steam-inlet line *m* on the side of the outer shell for steaming out. Also, a 3-inch outlet steam line *n* for steaming out is connected to the outlet vapor line and leads away to a sump. The arrangement of the vapor inlet *o* and the outlet *p* on the Gray tower is best shown by the cross-section *q* of the tower in the upper right-hand corner of Fig. 10. The tower has a manhead *r* at the top, through which the clay is charged,

also a manhead *s* on the bottom through which the clay is dumped. A safety valve *t*, as shown at the top of the tower, is set at 50 pounds. The tower is equipped with thermocouples and pressure gauges for determining temperatures and pressures of inlet and outlet vapors.

86. In the operation of the towers the vapors from the bubble tower are first sent directly through the condenser to the gas separator until the temperature in the bubble tower reaches 300° F. The vapors are then admitted into the Gray tower slowly, the outlet vapor line being kept closed until the pressure on the tower is up to normal; this is done to prevent channeling of the clay. When the vapors are introduced into the tower, the reflux and polymer lines are opened through the pot and the accumulator to a waste tank until the outlet temperature of the Gray tower is 300° F. This requires about an hour's time and is done to assure the removal from the system of all the water that may remain from the steam that was used in steaming out. The amount of such water is not large. The lines to the waste tank are then shut off, the automatic steam valve is started operating and the level is built up in the accumulator. The temperature on the bubble tower is next raised gradually from 300° F., to the normal working temperature of 325° F. This operation requires about an hour. The system is then held as close as possible to these conditions throughout the operation.

Should the stream of distillate from the condenser go off color in the middle of a run on the pressure still, it is necessary to connect the idle Gray tower. This operation is much the same as connecting a tower at the beginning of a run. The outlet on the cool tower is closed and the reflux and polymer lines are opened to the waste tank. The vapors are then gradually admitted into the Gray tower until the line is wide open. After closing off gradually on the vapor line to the used tower, the operator then proceeds as when connecting a tower at the beginning of a run.

87. Shutting down is also another important step in connection with the operation of a tower, especially when the run

is completed and the clay has not yet reached its maximum yield. After the heating of the still has been stopped, the vapors are left in the tower for 1 hour longer, the inlet and outlet vapor lines being closed. Usually there is one man at each valve and the valves are closed almost simultaneously. The automatic steam regulator on the reflux line is shut off and both the reflux and polymer lines are left open to permit draining of the tower. The pressure is allowed to fall 5 pounds, all the lines are then closed and the tower is left bottled up, ready for use in the next run.

When the clay is ready to be dumped, the tower is left bottled up as usual. About 20 pounds of steam pressure is then introduced into the tower and the steam outlet is opened to the sump. Steaming is continued for about 5 hours, or until the odor of the steam is no longer objectionable. To determine when the steaming is complete, the valve at the bottom of the polymer pot is opened occasionally after the tower has been steaming about the desired length of time, and the odor noted. When the operation is completed, the exhaust steam should have only a slight odor of gasoline. The tower is then unheaded, the clay is dumped into a truck and hauled to the filter plant for burning. Little difficulty is experienced in emptying the tower, since the clay is comparatively dry.

88. Through a Gray tower 11 feet in diameter and 16 feet in height, containing a layer of 30 to 60 mesh fullers' earth 8 feet thick, some refiners pass vapors at an average rate of 25 barrels per hour. The pressure drop through the clay bed is about $3\frac{1}{2}$ pounds and the temperature loss only about 5° to 10° F. In view of the small temperature drop, there is no difficulty in controlling the bubble tower to yield gasoline of the proper end point at the outlet of the Gray tower. The polymer fraction represents about 4 per cent. of the gasoline by volume and contains about 80 per cent. of gasoline and 20 per cent. of true polymer. In other words, the net loss due to polymerization is about .8 per cent. The yields of stable gasoline are dependent on the length of time that the clay has been in use.

Some refiners have found that it is advantageous to inject a solution of soda ash into the gasoline condensers in order to stabilize the product. This is because gasoline from Gray towers often contains an appreciable quantity of sulphur dioxide which, if not removed at once, is detrimental to the color stability of the gasoline. The Gray vapor-phase method makes unnecessary the ordinary acid treatment of pressure distillate. The gasoline from this process is finally sweetened by the sodium-plumbite treatment.

GASOLINE-RECOVERY SYSTEMS

89. Most refineries have in connection with their other refinery equipment, plants for the extraction of gasoline from uncondensed still gases. Such plants tend to reduce refinery distillation losses to a minimum. The three different types of plants that are used for this purpose are: compression plants, absorption plants, and a combination of the two.

The general process involved in the compression system for the extraction of gasoline consists in compressing the gases, by either single or double-stage compression, after which the compressed gases are passed through water-cooled coils where they are condensed. In the absorption process, the vapors are led directly to adsorbers, which are vertical towers in which baffles are placed. In these absorbers the gases pass counter-current to the flow of the absorbing oil, which may be a heavy naphtha or other oil suitable for the extraction of light gases. Intimate contact between the two is assured by the presence of the baffles in the absorbers. Greatest efficiency and highest yields are obtained by combining the compression and absorption methods, and this, therefore, is the most common practice in refineries. In nearly all cases, with any of the three methods mentioned, it is necessary first to scrub the gas for the removal of objectionable sulphur compounds before condensing it. Usually this is done by passing the gas through a series of baffled water scrubbers by means of which the free sulphur and part of the hydrogen sulphide are removed; then through a lye scrubber where the gases are washed with a solution of sodium hydroxide and, finally, through another water scrubber in which

the last traces of caustic soda are removed. Frequently, doctor solution is used instead of caustic soda. In some cases iron oxide, which is kept in suspension in water by agitation with air, is used for the removal of appreciably large quantities of sulphur and hydrogen sulphide. The gasoline recovered in the process is subsequently blended with other refinery gasoline either in the field storage tanks or in the accumulators, which are tanks that are under the same pressure as the coils in a compression system. In many cases, by a predetermined rate of pumping, the heavy naphtha used in the process is blended directly in the system to the point at which a marketable grade of gasoline is obtained.

REFINING OF HEAVY OILS

Serial 2292

Edition 1

METHODS AND MACHINERY USED

PRELIMINARY PROCESSING OF HEAVY OILS

WAX DISTILLATE FROM PARAFFIN-BASE CRUDE OILS

1. Introductory.—By heavy oils are meant lubricating oils, fuel oil, road oils, asphalt, and similar viscous products obtained from crude petroleum. Lubricating oils represent, by far, the most important of the products mentioned, because of the greater difficulties encountered in their manufacture and because of the uses to which they are put.

Briefly, the procedures involved in the manufacture of lubricating oils from crude petroleum are distillation; chemical treatment; treatment with absorbents, a form of filtration; dewaxing; and blending and compounding.

Distillation is an indispensable step in the manufacture of lubricating oils. Whether or not any or all of the other steps follow depends on the characteristics of the crude oil and the degree to which it is desired to refine the oil undergoing treatment.

2. Removal of Wax.—The residue that remains in the still after the separation of the gas-oil fraction from the crude oil, is called the wax distillate, and this is the starting point for the manufacture of the lighter-bodied lubricating oils.

The wax-distillate cut from the crude oil contains some wax that is in the crystalline form. However, for the most part, the wax is in the colloidal or amorphous form and, therefore,

at least part of this cut must be rerun in fire stills in order to crack the amorphous wax; that is to change it from the amorphous to the crystalline form, in which condition the wax is more readily separated in subsequent operations. Wax congeals at low temperatures, and it is on this fact that the refiner depends for the separation of the wax from the wax-distillate cut.

The oil from which the wax is to be removed is first cooled to about 20° F. and is then pumped through a filter press. The wax which separates, or crystallizes, from the oil is then retained by the filter cloth which covers each filter plate. For best results, the wax must keep its crystalline structure so as not to be forced through the cloth and in addition, the wax cake as it builds up must remain porous, so as to allow the oil to strain through it with no great diminution of flow.

3. Processing of 37° Distillate.—Some refiners, using fire and steam distillation, distil off approximately 55 per cent. of the crude oil as benzine and kerosene, and then make a cut called 37° distillate. This fraction consists of about 15 per cent. of the crude oil and contains enough crystalline wax so that it can be chilled and pressed satisfactorily without first being cracked in fire stills.

About 10 per cent. of the distillate, or 1.5 per cent., based on the original crude oil, is recovered as wax. The remaining oil, which is known as pressed distillate, accordingly amounts to about 90 per cent. of the 37° distillate or 13.5 per cent. of the crude oil. The pressed distillate is then returned to the still and redistilled, about 80 per cent. being converted into gas oil and neutral non-viscous oils, or oils that have a low viscosity. The remaining fraction, which represents about 20 per cent. of the pressed distillate, becomes a neutral oil of high viscosity. Stated more exactly, the non-viscous oil has a viscosity of less than 150 seconds on the Saybolt Universal viscosimeter and the viscous oil has a viscosity greater than 150 seconds. The number of seconds represents the time required for a given quantity of oil, at a predetermined temperature, to run from the containing vessel of the apparatus.

4. Cracking Distillation of Wax Distillate.—The cracking distillation of the raw wax distillate, or 34° stock as it is also called, which is a fraction from the crude oil, is carried out in fire stills using no steam at first and only a very small amount of steam at any time during the distillation. Benzine, kerosene distillate, gas oil, and cracked wax distillate are the products obtained overhead, while the bottoms, or residue, is pumped either to fuel-oil storage or back to the wax-distillate cut from the crude. In many cases, no kerosene-distillate cut is made, this being included in the benzine fraction, and the overhead distillates are divided into only three different cuts. The 34° stock represents about 10 per cent. of the crude oil, and after cracking and further processes the division, or break-up, is as shown in Fig. 1.

The viscosities mentioned in Fig. 1 are expressed according to the Saybolt system, which indicates the number of seconds required for a given quantity of oil at a given temperature to run through a standard orifice. Thus an oil might be said to have a viscosity of 275 seconds at 100° F. Commonly, the word seconds is omitted and the oil would be merely said to have a viscosity of 275 at 100° F.

5. The viscosity to which the viscous neutral oils are reduced may be varied to suit the market demand. In order to improve their color these oils, after being reduced to proper flash point and viscosity by distillation, are frequently filtered through fullers' earth; or, if necessary, they are treated with sulphuric acid, neutralized, and then filtered. The non-viscous neutral oils, of which several different cuts may have been made during the distillation of the pressed distillate, are returned separately to the fire-and-steam stills where they are further reduced, by use of little fire and much steam, until the residual oil possesses the desired physical characteristics. The viscosity of these non-viscous oils varies from 50 to 150 seconds at 100° F., on the Saybolt Universal viscosimeter. They, also, are usually filtered through fullers' earth as the final step in their refining. The oil remaining in the still after the fire-and-steam distillation of the crude oil may be sold directly

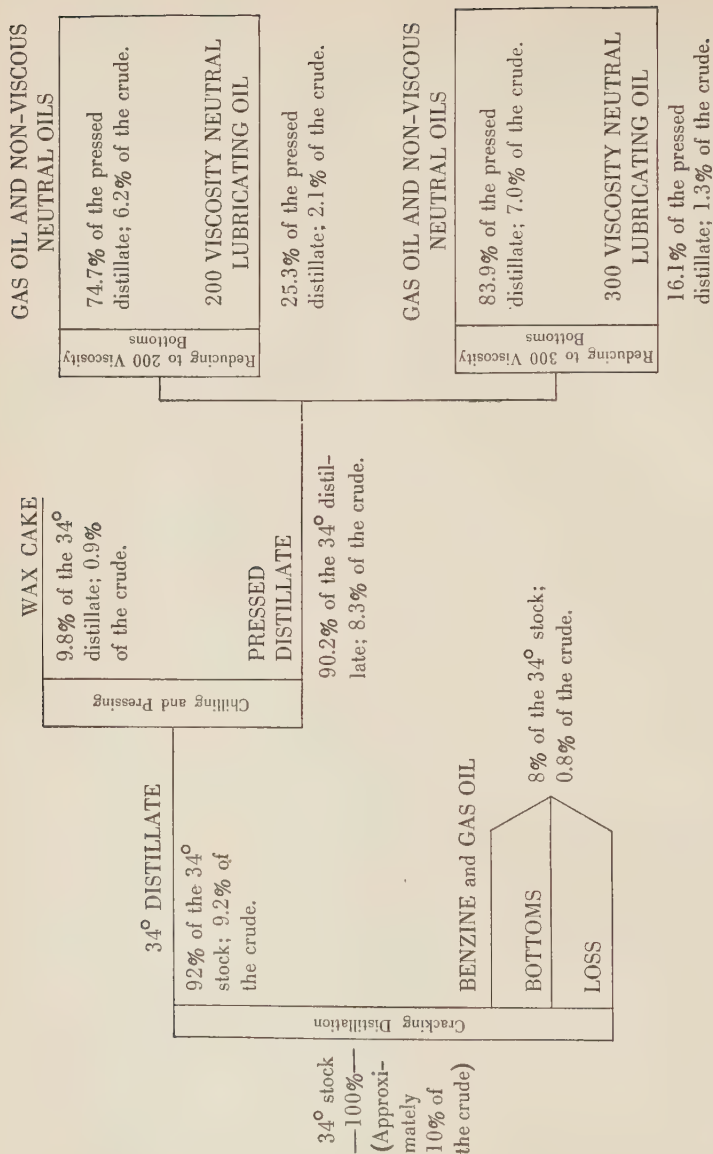


FIG. 1

as cylinder stock, if it is so desired. Or, it may be filtered through fullers' earth to improve the color, in which case it is then known as filtered cylinder stock. The extent of the distillation determines the physical characteristics of such oil. Bright stock is cylinder stock from which much of the wax has been removed by placing the oil in naphtha solution, filtering through fullers' earth to the color desired, chilling to a low temperature, and then allowing the mixture to cold-settle, in which case the wax settles to the bottom of the tank and the wax-free solution of oil is pumped off the top; or the wax may be removed centrifugally by the use of high-speed centrifugal clarifiers. In either process the diluted, dewaxed oil is then rerun in fire stills to remove the naphtha. The residual oil thus obtained is sometimes refiltered either to improve its color, or to remove moisture, or both, before being marketed.

PROCESSING OF MIXED-BASE CRUDE OILS

6. Fractionation of Crude Oil.—Not all mixed-base crude oils are suitable for the manufacture of lubricating oils. Relatively large quantities of both asphalt and paraffin are present in mixed-base crudes and, to make satisfactory lubricants from them, most of the compounds of asphaltic and waxy nature must be removed during the process of refining. This greatly increases the operating costs in making such lubricants. However, lubricating oils of good quality are made from mixed-base crudes and to such an extent that sole dependence on paraffin-base crudes, as the source of lubricating oils, is not necessary.

In the reduction of stripped crude or crude oil from which gasoline and kerosene fractions have been removed, to 14° to 16° gravity fuel-oil bottoms by batch operation, the following cuts may be made.

Over to 37° stream gravity.....	Rerun distillate
37° to 33° stream gravity.....	Gas oil
33° to 26.5° stream gravity.....	Raw wax distil- late; also called tube distillate
26.5° to off.....	Wax slop

By the term "over" is meant that point in the beginning of the distillation when the first of the condensate appears in the receiver.

At times, however, it has been found advantageous to take the following fractions:

Over to 35° stream gravity.....	Rerun distillate
35° to 34° stream gravity.....	Wax slop
34° to 29.5° stream gravity.....	Wax distillate
29.5° to off.....	Wax slop

It cannot be emphasized too strongly that the exact points at which the wax distillate and wax slop cuts are made, will depend on the crude that is being run, and what the past experience has been as to the physical characteristics necessary for the raw wax distillate to possess, so that, when blended in the proper ratio with cracked wax distillate, a suitable stock for pressing will be obtained. There is no regular temperature nor gravity at which the wax distillate first appears. Neither is it possible to foretell how long the stream will continue to show wax distillate of relatively low cold test, nor when the overhead product will tend to become excessively heavy in wax, as indicated by its mushy appearance and high chilling point. For this reason, the method of making the cuts must be changed to apply to the different crudes that are being refined.

The wax slop is cracked by batch distillation and thereafter blended with the raw wax distillate obtained from the primary distillation of the crude, in the proportions necessary to give a stock that can be handled to an economic advantage in subsequent operations.

7. Removal of Asphalt from Wax Distillate.—If the crude oil contains relatively large percentages both of asphalt and of paraffin, it frequently happens that a sufficient quantity of asphalt is present in the wax, or paraffin distillate, to cause operating troubles during the pressing of the chilled distillate. For this reason, the wax distillate is often treated in heavy-oil agitators with sulphuric acid before being transferred to the wax

plant. Treatment with from 8 to 10 pounds of acid per barrel of oil, at a temperature of about 150° F., is a frequent practice.

After the sludge resulting from the acid treatment has settled-out, the oil is pumped to an adjoining agitator. In this agitator the treated oil is neutralized with a solution of either caustic soda or soda ash, and then washed with hot water and steamed until all traces of alkali have been removed.

The wax distillate from the acid-treated, mixed-base crude oil is then processed in the wax plant in a manner similar to the practice followed in removing the wax from the wax-distillate cut of a paraffin-base crude.

The pressed distillate, as the wax-free wax-distillate cut is now known, is next reduced by a combined fire-and-steam distillation to bottoms of such viscosity as is economically advantageous. Reduction to a point where the residual oil has a viscosity of 275 seconds at 100° F. or 250 at 100° F. after acid treatment and filtration, is a common operating procedure. A few refiners reduce the pressed distillate to such a point that, after acid treatment and filtration, a viscosity of 180 to 100° F. will be obtained. A few others carry the reduction down to a bottoms having a viscosity of 390 to 400 at 100° F., in which case the oil, after being treated and filtered, will have a viscosity of about 350 at 100° F.

8. Fractionation of Pressed Distillate.—Different methods of fractionating the pressed distillate are in use in various refineries. Cuts are always made for either benzine (crude naphtha), rerun distillate, or all of these together with gas oil. Approximately 9 per cent. of the lighter distillates and 30 per cent. of gas oil are thus obtained from the distillation of pressed distillate. The number of different lubricating-distillate cuts, and the points at which such cuts are made, are varied in each refinery. The procedure followed depends on what is deemed advisable in order to obtain the maximum yield of the products desired at the lowest operating expense, and in order to suit practical conditions of operation within the plant itself. One method of making the cuts that is often used is as follows:

Over to 50° stream gravity.....	Crude-naphtha
50° to 38° stream gravity.....	Rerun distillate
38° to 30.5° stream gravity.....	Gas oil
30.5° to off.....	"30" pale distillate

The residual oil has a viscosity of either 220 or 275 at 100° F., depending on whether a finished oil with a viscosity of 200 or 250 at 100° F. is wanted.

The 30 pale distillate is then rerun by a fire-and-steam distillation, using much steam, and making cuts of the overhead distillate for gas oil and 30 and 28 pale oils, the oil remaining in the still is known as 25 pale oil. In the foregoing, the figures given, represent approximate gravities in degrees A. P. I.

Another method is to make three different cuts of the overhead lubricating distillate, as follows:

31.5° to 29° stream gravity.....	30 pale distillate
29° to 27° stream gravity.....	28 pale distillate
27° to off.....	25 pale distillate

These different cuts are then brought back separately to the still, where they are reduced to the proper flash point and viscosity test.

Still another method is to make cuts for 30 and 25 pale distillate in the distillation of the pressed distillate. The 30 pale distillate is then reduced to 28 pale oil, gas oil and 30 pale oil resulting from this distillation. To obtain the proper flash point and viscosity test, the 25 pale distillate is returned to the still, and reduced with fire and steam until physical tests show that the residual oil is at the point desired.

A fourth method is to make cuts for 30 and 28 pale distillate, and to reduce the former to a 28 pale oil, taking 30 pale oil off overhead as a distillate; and to reduce the latter to 25 pale oil, making a cut from the overhead distillate for 28 pale oil. Various other methods of making the cuts are possible. Laboratory tests, however, will determine just which methods are best. The laboratory plays an important part in controlling all the distillations involved in the manufacture of lubricating oils; for, in addition to the gravity of the stream, which the

stillman takes, viscosity, flash and fire tests are taken at regular intervals in the laboratory to aid in determining the point at which the various cuts shall be made.

The various viscous and non-viscous oils are transferred to the agitators, where they are treated with sulphuric acid, neutralized in a second agitator with a solution of either caustic soda or soda ash, washed with water, and then pumped into bleachers, where the moisture is removed and the oil thus brightened. Some of these different oils are sold under various trade names without any additional refining, but usually, as the final refining process, they are filtered through fullers' earth for the purpose of improving their color and removing any objectionable impurities.

As the finished oils are placed on the market, 30 pale oil has a viscosity of about 70 at 100° F.; 28 pale oil, a viscosity of about 100 at 100° F.; and 25 pale oil is a viscous neutral oil having a viscosity of about 150 at 100° F.

9. Batch Distillation of Green Crude Oil.—In the batch distillation of green crude oil or crude from which cylinder stocks can be made, cuts are made either for gasoline or light

TABLE I
PROPERTIES OF CYLINDER STOCKS

Properties	Cylinder Stocks From Pennsylvania Paraffin-Base Crudes	Cylinder Stocks From Mid-Continent Mixed-Base Crudes
Gravity ° A. P. I.....	24.0-27.5	18- 22
Flash ° F.....	500-625	490-575
Fire ° F.....	565-700	550-650
Viscosity (Saybolt) at 210° F..	120-250	130-250

or heavy crude naphtha, or all three of them, rerun distillate and, sometimes, gas oil. As a rule, the raw wax distillate and the wax slop are combined in one cut, and the whole is then rerun to yield a maximum quantity of cracked wax distillate.

The cylinder-stock bottoms, also known as S. R. or steam-refined stock, is marketed either as an untreated stock, or it is treated with from 30 to 40 pounds of sulphuric acid per barrel at a temperature of 160° to 170° F., and then neutralized with ammonia, after which it is sold as a treated cylinder stock. Or, if the treated oil is next placed in solution with filter-house naphtha, filtered through fullers' earth, and the wax then removed either by cold settling or by centrifuging, the oil after the naphtha is distilled off is marketable either as bright stock or filtered cylinder stock, depending on the color to which it was filtered. Typical finished cylinder stocks from paraffin and mixed-base crude oils have the properties given in Table I.

The limits given in Table I are applicable to treated and untreated, filtered and unfiltered, dewaxed and undewaxed cylinder stocks. Filtering tends to raise the gravity and lower the viscosity, but has little effect on the flash and fire point. Dewaxing tends to lower the gravity and raise the viscosity, the flash and fire point being the same, since the oil is brought to the same flash point in the reduction of the dewaxed solution of cylinder stock.

Residual oils from 390° to 490° flash point and viscosity of 75 to 115 at 210° F. are now usually spoken of as long residuums, and, after treating, filtering and dewaxing, are spoken of as sharp stocks.

10. Another method of distillation used for green crude oil, consists in the removal of the lighter products from the crude oil in two batteries of continuous crude stills, each battery consisting of five stills. Each still is fitted with suitable fractionating, or air-cooled, condensing towers, so that it is possible for all of the streams from the first three stills to go into the gasoline run-down tanks.

From the top of the fractionating tower of the fourth still, vapors are obtained which, after being liquefied by passing through the coils in the water-cooled condenser box, constitute the remainder of the gasoline fraction of the original crude oil. This product, if segregated, would not pass for gasoline, but would be classified as naphtha. However, when added to the

lighter products taken off in the preceding three stills, the whole combines to form a good grade of marketable gasoline. Other heavier vapors condense out at the bottom of the tower, the condensate being led through a separate pipe to the receiving house, where it is diverted to the kerosene run-down tank. In cases where the fourth still of a battery of five stills is equipped with two efficient towers, it is frequently possible to obtain gasoline from one tower and kerosene from the other.

The vapors from the fifth still consist of the remainder of the kerosene and part of the gas-oil fraction of the original crude. Those vapors, which on condensation form the remainder of the kerosene cut, are the more volatile, and therefore it is the gas oil which is liquefied in the air-cooled tower and led by a separate line to the receiving house, where it is diverted to the proper tank; while the kerosene vapors enter the water condenser for final liquefaction.

The residual oil, as pumped out from the fifth still of the battery, represents a stripped or topped crude oil; that is, a crude from which all the lighter fractions have been removed. It is from this oil that lubricating oil and wax are obtained. A frequent practice followed by refiners who manufacture cylinder and bright stocks from mixed-base crudes is to transfer this topped crude to the lubricating-oil agitators, in which it is treated with 20 to 30 pounds of sulphuric acid per barrel of oil. The treated oil is then neutralized with either ammonia or a solution of caustic soda or soda ash, care being taken during the process of neutralization, to avoid emulsification, and then is returned to the stills, where cuts are made for rerun distillate, gas oil, raw wax distillate and wax slop, a cylinder-stock bottom being left. The process of operation thereafter is almost identical in manner with that which previously has been described.

PROCESSING OF ASPHALT-BASE CRUDE OILS

11. Batch Distillation.—Asphalt-base crudes contain no wax and, hence, most of the refining of such oils is accomplished by simple fire-and-steam distillation at atmospheric pressures; or, as is the growing tendency, by distillation under vacuum.

Asphalt-base oils decompose more readily than do paraffin-base oils; hence, it is exceedingly important that the distillations be conducted either under vacuum or under conditions in which large quantities of steam are used in a combined fire-and-steam distillation of the oil. Asphalt-base crudes are distilled either in the conventional type of cylindrical still by continuous, semi-continuous or batch operation, or in pipe stills, by which the lighter products only are removed from the crude oil in a continuous operation. In the batch distillation of an asphalt-base crude petroleum, if naphtha is contained in the crude, it is first distilled off and collected in a run-down tank kept for that

TABLE II
FRACTIONATION OF CRUDE OIL

Fractions	Designation of Fraction	Per Cent.
Over to 30° gravity.....	Light gas oil	7.0
30° to 25° gravity.....	Heavy gas oil	26.4
25° to 22° gravity.....	Light lubricating distillate	16.1
22° to off.....	Heavy lubricating distillate	36.3
Bottoms	Road or fuel-oil stock	13.0
Loss		.4

purpose. Depending on market conditions, the next fractions distilled over are either separated into light and heavy gas oils, or these fractions may be combined into one cut and as such be allowed to flow into a gas-oil run-down tank.

The lubricating distillates, which are next separated from the crude, may be divided into only two fractions—light and heavy lubricating distillates; or into three fractions—light, medium, and heavy lubricating distillates. The practice is largely influenced by market conditions. Each fraction is stored in a separate run-down tank until ready for subsequent processing. A typical method of fractionation, during batch distillation, with fire and bottom steam agitation, is given in Table II.

12. The lubricating distillates are either separately returned to the stills and reduced to bottoms of the flash point

and viscosity test desired, and then treated and filtered to color, or they are redistilled, usually with from $\frac{1}{2}$ to $1\frac{1}{2}$ pounds per barrel of caustic soda in solution in the still, by either continuous or semicontinuous distillation, and cuts are made of the overhead distillates for lubricating oils of various viscosities. Much steam agitation is necessary during the distillation to prevent cracking. When the second process is followed, air-cooled, fractional condensing towers preferably are used to secure a good separation. By the first process, a greater yield of oils of high flash test is secured, and by the second method, which is the one most generally used, oils of better color are obtained, and less acid is required in their subsequent refining.

The untreated lubricating stocks are then transferred to the heavy-oil agitators, where they are treated with 10 to 20 pounds per barrel of either 66° Bé. or 98 per cent. sulphuric acid. After all the sludge has been drawn off, the oil is pumped to an adjoining agitator, where it is neutralized with a solution of either caustic soda or soda ash, washed with water, and then pumped to bleachers where it is blown with air until bright, that is, until free from moisture. After having been brightened, the oil is marketable. It may, however, be transferred to the filter house to be filtered to a lighter color and then marketed.

13. General Processing Procedure.—The general processing operation of an asphalt-base crude oil consists in skimming the crude oil of its lighter distillates by continuous distillation in two toppers, or pipe stills, each of which, for illustrative purposes, is assumed to be able to remove 500 barrels of oil from the crude as an overhead distillate every 24 hours. About 32 per cent. of the crude thus is removed as a light distillate, while the residual oil containing the lubricating-oil fractions is rerun in the conventional type of horizontal stills. The light distillate is rerun, and all of the overhead distillate, so long as the color is good, is put into the naphtha run-down tank. This is acid treated and sweetened in the agitators before it is marketable as a gasoline blending naphtha. Gas oil is the product remaining in the still at the end of the distillation. Cuts are made in the distillation of the crude bottoms for gas oil, and

light, medium and heavy lubricating distillates, while the residual oil in the still is a fuel-oil blending stock. Marketable fuel oil is made by blending this fuel-oil stock with gas oil. The light lubricating-distillate fraction is rerun, and cuts are made therefrom for light distillate and gas oil. The distillation is continued until the oil remaining in the still is of such viscosity that, after acid treating and filtering, it will have a viscosity of 200 at 100° F. In rerunning the medium lubricating distillate, cuts are made for light distillates, gas oil and light lubricating distillate, while the residual oil is of such viscosity that, after acid treating and filtering, it will have a viscosity of 600 at 100° F. Gas oil, light lubricating distillate, and 600 red stock are the cuts made from the overhead distillate in rerunning the heavy lubricating-distillate fraction. Fuel-oil blending stock is the residual oil from this distillation. In all cases, the product obtained from any distillation after the primary distillation, if similar in characteristics to a product resulting from a preceding distillation, is combined with that other product, and, if it is either advantageous or necessary to do so, the whole is rerun. For example, a light-distillate fraction is obtained from the primary distillation of the crude. A cut similar in characteristics is obtained from the rerunning of both the light and the medium lubricating-distillate fractions. These light-distillate cuts from all sources are then rerun to yield blending naphtha and gas oil. In a like manner, all other cuts (resulting from the distillation of different products) that are similar to each other in their physical properties, are combined into one cut and are later rerun.

VACUUM DISTILLATION OF ASPHALT-BASE CRUDE OILS

14. Advantages of Vacuum Distillation.—The growing tendency in refining asphalt-base crude oils is to carry out either the primary or the secondary distillation, or both, under vacuum. The advantages of this method of separation over fire-and-steam distillation are found in the reduction of the tendency of the oil to decompose, or crack, since the boiling point of the oil is materially lowered below that existing in a fire-and-steam distillation. Lubricants of superior quality are therefore produced,

and fuel consumption and the area of condensing and cooling surface is greatly reduced. Also, when distillation is carried out under diminished pressure, about 4 per cent. greater yield of products from the distillation operation is obtained, partly because of a reduction in treating losses. A further saving of 50 to 75 per cent. in the amount of sulphuric acid used is also ordinarily effected.

15. As already mentioned, lowering of the boiling point of an oil below the critical temperature at which that oil would begin to decompose can be accomplished by injecting steam into the liquid, by diminishing the absolute pressure in the condensing equipment, and by the simultaneous employment of both means; that is, by diminishing the absolute pressure in the condensing equipment, and, at the same time, injecting steam into the liquid to be distilled.

The primary purpose of injecting steam into the oil is to diminish the tension of the oil vapors, thereby decreasing the boiling point of the liquid. In this respect steam serves a purpose similar to that of an air pump; namely, the steam thus introduced within an oil body is a means of reducing the pressure, although the physical procedure is different. In the second place, the introduction of steam into a body of oil in a still effects an active circulation of the liquid and thus avoids local overheating.

Two principal objectional conditions exist in the combined fire-and-steam distillation either of crudes containing lubricating-oil fractions or of intermediate lubricating distillates. These are: First, when excessively large quantities of steam are required to accomplish the desired results, costs of distillation are increased too greatly. Second, the injection of large volumes of steam into the oil, lowers the quality of the distillates produced, because in the emergence of very great quantities of steam from the evaporating surface, considerable quantities of undistilled liquid particles are mechanically carried over into the distillates. As a result of this condition, the subsequent chemical treatment of the oil is rendered much more difficult and expensive. Further, large losses in treatment result. Of

course, the proportion of particles carried over mechanically can be reduced by the use of liquid separators (mist extractors), but it can never be wholly eliminated. Reduction of the distillation capacity naturally affords a remedy, but this results in inadequate utilization of the equipment. Consequently, in recent years, refiners, particularly refiners of asphalt-base crude oils, have been turning toward vacuum distillation, either with or without the additional aid of small quantities of steam, as a solution to the problems encountered in ordinary fire-and-steam distillation at atmospheric pressure.

16. Schulze Process.—The equipment used in the Schulze process of vacuum distillation, consists essentially of a still with internal bracing, about 9 feet in diameter and 30 feet long with welded seams and dished heads, and having a capacity of 320 barrels when completely filled. Instead of resting on the brickwork of the still setting, where the weight is likely to result in buckling and cracking of the walls, the still is suspended from overhead structural-steel supports. The furnace is heated by two oil burners, but, instead of these being placed in the usual manner in the center of the face of the furnace where the flames shoot out directly into the combustion chamber and against the fire-sheet of the still, they are placed one on either side of the furnace. The flames from the burners shoot into tunnels 18 inches wide by 24 inches deep, which are located on each side of the furnace. These tunnels run the entire length of the furnace and still, and connect with the flue and stack. The walls of the tunnels are built of firebrick laid in fireproof cement and are perforated along the sides. The flat tops of the tunnels also are perforated with oblong holes just large enough so that each may be covered by a firebrick laid on top of it. As the flame traverses the tunnels, the heat is radiated through the holes into the furnace under the still. By this method the flame is prevented from striking the still. If this precaution were not taken, the direct application of the flame to the still would cause local overheating, cracking of the oil, and early failure of the still-bottom. When the furnace in a new installation is started, all the holes in the tops of the tunnels are closed with firebricks,

while the draft is regulated by removing a sufficient number of bricks to give efficient combustion. The entire furnace is lined with a thick layer of fireproof cement, which is pounded into place while in a damp, coarse, powdered form, after which it solidifies to the hardness of concrete.

17. Instead of having a single vapor dome, as do lubricating-oil stills for ordinary atmospheric distillation, the stills used in the Schulze process each have ten vapor domes of large size, spaced at equal distances along the top of the still. Each of the vapor lines is insulated heavily to prevent condensation, and slants downwards from the still instead of toward it, thus making reflux impossible. The joint from the upright to the horizontal part of the line is a square elbow, discouraging condensation by offering less surface than a rounding joint. The vapor lines pass to the condenser where each is joined through a reduction connection with its own 4-inch coil, which is cooled by water in a conventional condenser box. The purpose of having a number of vapor lines is to offer the easiest and most direct outlet possible to the vapors, thereby preventing turbulence of the liquid when the vapors attempt to escape therefrom, which condition causes cracking of the oil. Vacuum lines connect the stills, through six horizontal, internally-braced run-down tanks, to an electrically driven, two-stage, single-cylinder, dry vacuum pump. Any tank can be cut out of the system at any time and the vacuum released. Schulze stills are further equipped with special apparatus by means of which the non-condensable gases and harmful organic compounds are withdrawn and separated during the distillation.

18. The Schulze process is especially applicable to the distillation of a topped, asphaltic-base crude oil. For best results, however, the stripping or topping (separation by distillation of all lighter products of the crude down to the point at which lubricating-oil fractions distil over), should be conducted in such a manner as to avoid cracking any of the heavier products. Then, 240 barrels of topped crude is charged into the 320-barrel still. By means of the main vacuum pump the pressure in

the entire system, including the still, the condenser, and the particular receiver connected therewith, is reduced to below 5 millimeters of mercury absolute pressure. To accomplish this, however, absolutely-tight apparatus throughout is required. The temperature of the oil in the still is then brought up gradually to the initial distillation temperature which, in the case of a topped crude, usually ranges between 300° and 350° F. If the oil to be treated contains water, the still should be gradually heated up before being placed under high vacuum. The temperature of the oil in the still is under observation at all times by means of a pyrometer, which may be so located that the thermo-couple is within a half inch or so of the bottom of the still at a central point therein. The temperature of the oil in the still may be closely controlled by regulation of the firing flame. As soon as distillate begins to come over, a sample is taken and its viscosity is determined. Meanwhile, the distillation continues, samples being taken at suitable intervals, until the increase in viscosity indicates the necessity or desirability of cutting the distillate into a second receiver. For example, if it is desired to make spindle oils, the first cut can be made when the distillate shows a Saybolt Universal viscosity of 100 seconds at 100° F. The pressure in the first receiver may then be released and the first cut pumped to storage. Substantially the same procedure is followed during the remainder of the distillation, the distillate being cut for the desired fractions in accordance with the increase in viscosity as determined by the testing of samples at frequent intervals. By this procedure, products totaling from 80 to 95 per cent. of the volume of the topped crude originally charged into the still may be obtained as straight overhead distillates. The residue is a flux oil having a gravity of about 12° to 14° A. P. I. The final distillation temperature, ordinarily, should not be allowed to exceed 620° to 630° F. as a maximum.

19. Another mode of procedure consists in making only two cuts in a first distillation of the starting material, the first cut being made when the distillate has attained a viscosity of about 750 seconds at 100° F., and then cutting the remainder

of the distillate into a second receiver. The first cut therefore includes all the lubricants up to and through grades of oil of the viscosity of heavy motor oils; the second cut, through both grades of the viscosity of extra heavy motor oils and also the heaviest lubricating oils up to a viscosity of as high as 170 seconds at 210° F. Sufficient quantities of these two cuts are accumulated to enable redistillation or rerunning of the cuts separately in rerun stills provided for this purpose. In rerunning the cuts, still narrower cuts are then made corresponding to the various commercial grades of oils for which there is a demand. This method of rerunning has the advantage of giving products of even better color than those obtained by the method of distillation first described. Consequently, the viscosity ranges of the various products obtained, respectively, are somewhat narrower.

20. Zieley Process.—The Zieley vacuum unit consists of pipe coils, separating chambers, economizers, fractionating towers and such similar equipment as is used in latest refinery practice. In this process, the charging stock is transferred to the vacuum unit at a temperature of about 140° F. It passes through the condensers and acts as a cooling medium, picking up the latent heat from the fractions that have just left the main body of the oil. When the crude oil leaves the condensers, it has already reached a temperature of about 360° F. It now passes to the economizer, situated in the main gas passage to the stack. Here the oil picks up additional heat, its temperature being about 475° F. when it leaves the economizer. It is discharged from the economizer into a specially designed separator, which is carried under a high vacuum. At this point about 25 per cent. of it flashes into vapor, which passes to the first condenser. The balance of the charge is then pumped to the upper tier of a bank of tubes. Each of two banks common to each unit is composed of 10 stacks of 4-inch tubes, each 20 feet long, placed at a slight angle from the horizontal. The tubes enter headers at this angle and zigzag back and forth, so that the bank takes a flattened **Z** shape. There are six tubes side-by-side forming each of the top five stacks of a bank and four tubes for the

lower five stacks. In the second bank there are three tubes for each of the five top stacks, the bottom half being made of two tubes each. The reduction in the number of tubes is due to the decreased amount of liquid flowing through the still as the distillation proceeds. The oil flows through the ten stacks by gravity, the stream being about a quarter-inch thick and the speed averaging, as estimated, 70 feet per minute, the entire operation being completed in about 15 minutes. The cascading of the oil from the ends of the tubes into the headers is said to be effective in bringing about the desired turbulence to assist in the rapid release of the vapors. The vapors are taken off instantly, as produced, at the forward five headers and are conducted to the second, third and fourth condensers. The charge is then pumped from the bottom of the first bank of tubes to the top of the second bank and flows by gravity through these tubes, five more vapor cuts being taken off at the turbulence-producing headers and combined in the fifth and sixth condensers. The residue is then pumped from the bottom of the second bank to storage. The entire tube still and the condensers are carried under high vacuum. Twenty-six separate streams are taken from the condensers, which are located well up in the air. The bleeders from the condensers are connected with blending lines and the blends of the distillates pass through cooling coils by gravity to look boxes of special form and then to the run-down tanks.

The flue gases, after leaving the tube still, contain a considerable amount of heat, and to prevent its loss up the stack, the economizer, which is of conventional design, is utilized. The separator is jacketed by the warm flue gases after they leave the economizer, and these same gases also pass through tubes running lengthwise through the inner compartment of the separator. These special features, combined with the fact that no head of liquid is allowed to build up in the separator, make it possible to take off a remarkably clean cut from the oil that is passing through the economizer. The total fuel consumption of the unit is very low, being only about 2.5 per cent. of the total charge when 60 per cent. of the charge is being distilled off.

21. The high quality of the products distilled in the Zieley unit is due to the high vacuum, with the consequent low temperature in the tubes of the still; the thinness and the speed of the stream while being subjected to the vacuum and to the heat exchange; the great rapidity of vaporization and the instant removal of the vapors; and the low cold-test, in oils containing paraffin, due to the short time of exposure to heat.

The foregoing features result in clean lubricating distillates that have no cracked or decomposed particles. As a consequence, the lubricating distillates from all crudes are bright and clear and need no further treatment to prepare them for sale. The subsequent preparation of these distillates for medicinal or other highly technical uses is carried on much more easily and at less cost, and with but a fraction of the former loss of product.

CHEMICAL AND PHYSICAL TREATMENT OF LUBRICATING OILS

CHEMICAL TREATMENT

22. **General Remarks.**—Distillation is the first and most important step in the manufacture of lubricating oils from crude petroleum; acid treatment, filtration and, in the case of paraffin or mixed-based crudes, dewaxing, are additional stages in the refining process. Crude oil is a mixture of different compounds or hydrocarbons in a pure state, plus certain other compounds or complex hydrocarbons, which, because of their characteristics and the fact that their presence in the finished product is detrimental thereto, may be classed as impurities. The problem of the refiner therefore involves the separation of these products or compounds from each other and the removal of the impurities, by various refining methods, from the separated components of the crude oil. Distillation, as a matter incidental to its chief accomplishment, partly segregates the objectionable asphaltic constituents into the heavier, or lubricating, distillates and residues, from which these impurities are finally removed by chemical treatment and filtration. Waxes, also, are undesirable in lubricating oils and, hence, in the manufacture of lubricating oils from paraffin or mixed-base crudes, the waxes are

separated from the oil by processes involving either filter-pressing or centrifuging, after the oil has been chilled by artificial refrigeration in order to solidify the wax.

23. Purpose of Chemical Treatment.—The general purpose of treating lubricating oils with chemicals is to effect the removal of certain impurities. If the oil is not made free of these impurities, its commercial value is diminished. Specifically, these impurities, which are either already present in the crude or else are formed during the distillation process, are mostly organic bodies containing sulphur, oxygen or nitrogen. That is, they are either asphaltic or bituminous substances that discolor the oil, or they are sulphur alcohols, pyridines, and other organic substances that give the oil an objectionable odor. By chemical treatment, then, a lubricating oil of lighter color when examined both under transmitted and reflected light is made, and any free carbon or carbonaceous matter in the oil is removed. In other words, a general purification of the product results.

24. General Method of Chemical Treatment.—Treatment with sulphuric acid followed by neutralization with a solution of either caustic soda or soda ash continues to be the general method used by refiners in the chemical purification of lubricating oils. Briefly stated, this operation consists in mixing the acid (usually in several doses) with the oil by means of air, inert-gas, or mechanical agitation. The acid reacts with the impurities in the oil to form a sludge, which settles and is drawn off from the bottom of the agitator. At this stage the acid oil is either neutralized by the so-called contact filtration process or it is pumped to a second agitator and therein neutralized with a solution of either caustic soda or soda ash. The chemical treatment of the oil is then completed by washing with water until all excess alkali and alkaline-reaction products have been removed, after which the oil is pumped to a storage tank or a bleacher tank. In the bleacher, traces of moisture are removed and the oil is brightened by heating and blowing with air at the same time.

25. Construction of Lubricating Oil Agitators.—Agitators for treating heavy oils are similar in outward appearance to light-oil agitators. Lubricating-oil agitators, however, are seldom constructed in capacities exceeding 2,500 barrels. Agitators of 1,000 barrels capacity are common and most agitators for treating heavy oils will come within the range of from 500 to 1,500 barrels in size. The general procedure among refineries is to treat the oil in one agitator with sulphuric acid and to neutralize and wash the oil with water in a second agitator. Whereas formerly it was common practice to line the inside of the agitator in which the acid is applied with sheet lead, in latest methods of construction this is not commonly done. The steel plates of the agitator are but little attacked by acid of 66° Bé. strength; instead, such plates are more readily corroded by weaker acid. Hence, if reclaimed acid is to be used in treating the oil, it is usually advisable to use a lead-lined agitator. Because of the possible presence of weak acid, wash agitators require lead linings. In order to avoid the possibility of sludge deposits in the cone of the agitator, it should be of ample size and its pitch should be not less than 45 degrees. Since the acid sludge resulting from the treatment of lubricating oils is very thick and viscous, no restrictions of opening should be allowed and an outlet diameter of from 12 to 24 inches is advisable. Because there is scarcely any fire risk in handling lubricating oils, steel globe roofs of medium depth are satisfactory for the acid agitators. With the wash agitators, however, moisture condensation on the under side of the roof is objectionable, and so often is of such seriousness that some refiners, to overcome this difficulty, build the agitators without roofs and place them in a building. Another satisfactory arrangement that accomplishes this same purpose is to support concrete roofs, independent of the wash agitators, upon the tile insulating jackets. Since lubricating oils are generally treated at temperatures of from 130° to 170° F., the shells of the agitators should be insulated in order to insure speed and control, as well as operating economy. The insulating jacket frequently is made of hollow tile or of hollow brick, and in order to avoid cracking from vibration, is so constructed as not

to touch the agitator shell, an air space of 4 to 6 inches being left between the shell and the jacket. Closed steam coils placed under the cone and between the jacket and the shell are frequently used to maintain the desired temperature on the oil undergoing treatment in the agitator.

26. Efficiency of Acid Treatment.—The chemistry of the sulphuric acid treatment of lubricating oils is so complex and so little understood that scarcely more can be done than to hazard a guess as to the reactions that take place. It is definitely known, however, that acid sludge contains both true reaction products and mechanically-entrained or absorbed substances that are brought down by the settling of the sludge. The kind of acid treatment to be used depends entirely on the characteristics of the product being treated, the type of crude from which such product was obtained, and the degree of refinement desired. The efficiency of the acid treatment depends on the temperature at which the treatment takes place, on the method of mixing acid and oil, the amount of acid used, and the length of time the acid and oil are in contact.

Generally the acid is applied to the oil when the latter is at the lowest temperature consistent with having the oil fluid enough to insure intimate contact with the acid. Agitation by means of compressed air is the common practice in mixing the acid and oil. The use of air is objectionable, however, because of its tendency to oxidize the oil, but nevertheless it is used generally because it is rapid, thorough and relatively cheap. The number of times acid is introduced and the amount of acid used in each portion, is determined by laboratory experiment. Thus, it is learned how to vary the number of acid dosages and the amount of acid on each dose so as to obtain a maximum decolorizing efficiency from a given amount of acid. The length of time the acid and oil should be in contact, in order to utilize the full value of the acid, depends on the method and violence of the agitation, the size and shape of the agitator, the viscosity of the oil, the quantity of acid used, and the number of portions in which the acid is applied to the oil.

The grade of acid most generally used in the treatment of lubricating oils is 66° Bé. sulphuric acid, which contains 93.19 per cent. of acid. Acid of 98 per cent. strength, however, has been found by many refiners to be more efficient than 66° acid, particularly so in the treatment of asphalt-base lubricating oils. Acid recovered from acid sludge, of 60 to 65° Bé. gravity, is frequently used in the preliminary treatment of some lubricating oils.

27. Emulsification During Acid Treatment.—Emulsification of the oil during treatment may be caused by an excess of acid in the oil when the alkali was added, by undue agitation, or other careless handling of the batch in the agitator, and by peculiar and unexplainable characteristics of the lubricating distillate itself. Emulsions usually can be broken up by adding acid in excess of the neutralization point, by the addition of alcohol, by heating to higher temperatures, and by the use of special, patented demulsifying agents.

Because pure paraffin-base crudes are relatively free from asphaltic constituents, few of the lubricating oils made therefrom require treatment with sulphuric acid. Lubricating oils from mixed or asphalt-base crudes, however, do require purification with acid. Types of lubricating oils usually treated with acid are:

1. Paraffin or wax distillate.
2. Non-viscous neutral or paraffin oils. These are oils below 150 seconds viscosity at 100° F., obtained from the distillation of pressed distillate, which is the wax distillate fraction made free of paraffin wax.
3. Viscous neutral or paraffin oils. These are oils from 150 to 300 seconds viscosity at 100° F., obtained from the distillation of pressed distillate.
4. Cylinder stocks, or residual oils with a flash test of from 500° to 600° F.
5. Long residiums, or residual oils with a flash test of from 390° to 500° F.
6. Stripped crudes, or residual oils from which gasoline, kerosene and some gas oil have been removed.

7. Pale oils from asphalt-base crudes.
8. Red oils from asphalt-base crudes.
9. Slack wax and crude scale wax.

28. Treatment of Wax Distillate.—Wax distillate is treated with acid and lye only in those cases when the wax distillate contains asphaltic constituents in such an amount as to interfere with the efficient separation of the wax in the presses, unless the oil were so treated. Wax distillate is treated at a temperature of from 130° to 150° F., with about 8 to 10 pounds of 66° sulphuric acid. After the sludge has settled and been drawn off, the oil is transferred to a second agitator where it is neutralized with a weak solution of caustic soda or soda ash, and thereafter washed with hot water until free from alkali, as shown by the use of phenolphthalein indicator. A sample of the oil from the agitator, when mixed in a 4-ounce bottle with an equal amount of water and a few drops of phenolphthalein solution, will show pink in the water layer if alkali is present, but will remain colorless if free alkali is absent.

29. Treatment of Non-Viscous and Viscous Paraffin Oils. If the non-viscous paraffin oil has any water in it after it has been pumped to the agitator, as is indicated by a lack of transparency, the water must be removed before the main acid treatment is applied, as the presence of water in the oil is detrimental to the efficiency of the acid treatment. The water is removed by a so-called water-acid dump; that is, by agitating the oil for from 5 to 10 minutes with from $\frac{1}{2}$ to 1 pound of acid per barrel of oil. Sometimes several small dumps of acid are required to remove all the water. A frequent practice is to apply small water-acid dumps until, after the mixture has settled for from 1 to 3 hours, a small amount of sludge but no water is thrown down. Then it is absolutely certain that no water is in the oil.

The main acid treatment is applied to the oil in either one or two dumps, depending on what the previous experience has been as to the procedure by which most efficient results are obtained. From 4 to 16 pounds of acid per barrel of oil is the total amount of acid generally used on oils of this class.

When the acid is applied in two dumps, such dosages are usually equally divided. After the oil has been agitated with the main acid dump for about 30 minutes, a sample is taken from the agitator, filtered, and examined for color. If the oil is not of the desired color, more acid is added and the treatment is continued. When the color of the oil is satisfactory, the acid sludge is caused to settle by sprinkling the oil, during agitation, either with water or with a weak solution of caustic soda or soda ash. If the oil is one from which the sludge settles quickly, water is the best medium to use.

In settling, or breaking, any batch, water or alkali solution is added in the smallest quantities necessary to get the minute particles of sludge to collect into lumps. A heavy oil that contains a large amount of sludge may gather into lumps as large as a pea. Lighter oils contain less sludge and require more water to break them; furthermore, the lumps of sludge from such oils are often only the size of a pin head. Breaking the batch, as described, makes possible quicker and more complete removal from the agitator of the reaction products of the treatment. During settling, the treater keeps drawing the sludge from the bottom of the agitator, as otherwise it is apt to solidify and to clog up the bottom opening. The time of settling depends on the judgment of the treater, and may vary from 2 to 14 hours.

When all sludge has settled from the oil, the latter is transferred to a second agitator and neutralized with a weak solution (1° to 5° Bé.) of caustic soda or soda ash. The lye solution is placed in the wash agitator before the acid oil is transferred. After neutralization has been completed, as indicated both by the appearance of the batch and by the reaction of a sample to phenolphthalein indicator, the batch is allowed to settle for 3 to 6 hours. The excess lye and salts are then drawn off, after which the oil is washed with hot water at about 150° to 160° F., until freed of excess alkali. It is then allowed to settle and next pumped to bleachers where it is heated and blown bright.

Some refiners soap their oils during or following the chemical treatment. The addition of naphthenic soaps removes from

the oil certain emulsifying constituents that are a product of the chemical treatment, and by this removal, oils of better quality result. In Table III are shown approximate temperatures for handling oils of various viscosities during the treating process:

30. Treatment of Cylinder Stocks and Long Residuums. The same general principles are involved in treating cylinder stocks and long residuums as in the treatment of paraffin oils.

TABLE III
VISCOSITIES AND TREATING TEMPERATURES

Saybolt Viscosity of Oil at 100° F. in Seconds	Temperature of Oils When Acid Is Added °F.	Temperature of Oil and Wash Water During Washing and Settling Period ° F.
50	70- 80	110-120
75	80- 90	120-130
100	85- 95	130-140
150	90-100	140-150
200	95-105	150-160
300	100-110	155-165
500	105-115	160-170
1,000	110-120	165-175
1,500	110-120	165-175
2,000	115-125	170-180

The main differences are that more acid, about 24 to 50 pounds per barrel, is required; higher temperatures, 130° to 170° F., are required for treating, depending on the viscosity of the oil; collection of the sludge by breaking with water is less often necessary; and neutralization with 1½ to 4 ounces of 26° Bé. ammonia, per barrel of oil in a second agitator, and no washing, since the addition of water would cause emulsification, is a common practice.

The contact-filtering process, whereby oils are simultaneously neutralized and decolorized, in many plants, is replacing the neutralization of cylinder stocks with ammonia. Other practices include treating the oil in kerosene solution, which makes

possible subsequent neutralization with solutions of caustic soda or soda ash.

Stripped or topped crudes or residual oils made as a preliminary stock for the manufacture of lubricating oils, are usually treated with acid and lye in a manner similar to the treatment of paraffin oils. Thereafter, they are rerun, wax distillate being one of the overhead products, and there are left in the still either long residuum or cylinder stock as a

TABLE IV
VISCOSITY OF OIL AND ACID REQUIRED

Kind of Oil	Saybolt Viscosity at 100° F. in Seconds	Amount of Acid in Pounds per Barrel	Strength of Acid
Pale Oil	70	8-10	66° Bé.
Pale Oil	100	10-12	66° Bé
Pale Oil	200	16-18	98%
Pale Oil	300	16-18	98%
Pale Oil	750	18-20	98%
Red Oil	200	8-10	66° Bé
Red Oil	300	8-10	66° Bé
Red Oil	500	10-12	66° Bé

residual oil, which is treated according to one of the methods already described.

31. Pale and Red Oils from Asphalt-Base Crudes.—In Table IV are shown the approximate quantities and strength of acid suitable for treating asphalt-base oils of different viscosities:

Asphalt-base lubricating oils are more difficult to treat than oils of similar viscosity made from mixed-base crudes, and efficient treatment demands all the skill and experience of the treater, particularly in avoiding emulsification during the neutralizing process. Preliminary distillation of asphalt-base lubricating oils over caustic soda, placed in the first still of the continuous battery when the lubricating distillate fraction from the crude oil is rerun, facilitates the acid treatment.

32. Reduction in Viscosity Due to Acid Treatment.—Oils after treatment with sulphuric acid are always lower in viscosity than the original oil, because the asphaltic matter removed by the acid is more viscous than the mixture of hydrocarbons composing that particular oil. In refinery practice, allowance is made for this loss in viscosity by having the oil before treatment more viscous than the oil desired as a finished product. For example, if a treated and filtered oil of 200 seconds viscosity were to be made from the pressed distillate from mixed-base crude, the oil would be reduced in the still to a viscosity of about 218 to 220 seconds at 100° F. and, as such, would be acid treated. Actual experience with a particular oil is the only criterion as to how much drop in viscosity will result from any given acid treatment and, hence, how much allowance must be made.

ACID SLUDGE

33. Handling of Acid Sludge.—The amount of sludge that results from the treatment of lubricating oil with sulphuric acid will vary from as low as 3 per cent., in the case of sludge from the treatment of non-viscous lubricating distillates, to as high as 35 to 40 per cent., in the treatment of cylinder stocks. Disposal of this sludge is one of the most serious problems with which the refiner must deal. Dumping this material into a pond or attempting to discharge it through the usual outlets for sewage soon creates an intolerable nuisance. In the past, large quantities of sludge have been burned in open ponds with no attempt to utilize the calorific value of the sludge. More recently, furnaces of special design have been employed for handling the sludge as fuel. So, too, improvements both in burner design and in technique of firing furnaces has made it possible to burn certain classes of sludge under boilers and stills, with fair efficiencies. However, the nuisance resulting from soot and fumes makes such practice unpopular in thickly settled communities.

Modern refinery practice consists in separating the acid from the acid sludge, concentrating the recovered acid for reuse and utilizing the neutralized sludge, usually as fuel. Paving asphalt and other special products can also be made from it.

The composition of acid sludge is very complex and it is difficult even to conjecture of what it consists. It is known, however, that it varies in its composition and characteristics depending on the nature of the oil being treated, the method of treatment, and the quantity and strength of the acid used in the treating process. Briefly, though, acid sludge may be classified as being an emulsion or solution of tarry matter in unspent acid which, in turn, holds in solution sulphuric addition products.

34. Separation of Acid from Acid Sludge.—The recovery of free sulphuric acid from the dark-colored, viscous, tar-like liquid or sludge discharged from the agitators, necessitates a separation of the acid from the oil and tarry products. The sulphonic acids contained therein are usually decomposed by diluting the sludge with an equal volume of water, heating the mixture to about 180° F. and then agitating the whole with high-pressure steam and air until no more sulphur dioxide is given off. By this cooking process, most of the sulphonic acids are broken up. The resulting sulphuric acid can then be concentrated to any desired strength up to 66° Bé. without further treatment.

The equipment required for acid separation naturally depends on the character and quantity of material to be handled. The sludge is diluted and cooked in lead-lined vessels or separators which are equipped with open steam coils and draw-off connections for oil and acid. The separators may be built with either a cone-shaped or a slanting bottom to suit local conditions and they should be placed in an elevated position to permit the separated material to flow by gravity into the acid run-down tanks. Ample storage should be provided for the weak acid, since only well-settled skimmed acid should be fed to the concentrator.

The size of the separator used depends on the size of the oil agitator that it serves, but it generally varies from 100 to 300 barrels in capacity. A separator of the latter size would serve satisfactorily a 1,000-barrel agitator. It is advisable to have at least one-third excess capacity in the separator. The separators are lead-lined and are also equipped for agitation

either with air or live steam. Separators 15 feet deep and 15 feet in diameter are of a size frequently used by refiners. The contents of the separator are heated either by the direct introduction of live steam, or by closed steam coils placed within the kettle proper or by both. All steam and air lines are made of lead. Because of the fact that complete separation of the acid may require as much as two days' time, it is usually advisable to employ two separating tanks for use with an agitator in which one batch of oil per day is treated; and four tanks, if two batches are treated in the agitator each day. The separators are equipped either with a lead plug, about 4 inches in diameter, which fits into the draw-off at the bottom, or with a valve made of some acid-resisting material. In the former case, the plug is raised to discharge the separator by pulling down on a chain that is attached to a lever which, in turn, is fastened to the top of the plug rod. The viscous tar-like liquid that settles out of the treated oil is either pumped from the agitator to the separator or is blown out with live steam. The draw-off pipe may or may not be steam jacketed. The disadvantage of not having a steam-jacketed line lies in the fact that when live steam is used in blowing the sludge from the agitator to the separator, there is a tendency for the condensed water to dilute the acid and a subsequent inclination of the acid to attack the pipe more readily.

35. Typical Methods of Separation.—In one process practiced by some refineries, the sludge when run into the separator is heated both by means of a closed steam coil and by blowing live steam directly into it until it is liquefied. This condition can be determined by punching around in the separator with a long stick. The contents are then allowed to settle for one or two hours at a temperature ranging from 150° to 200° F., after which the greater portion of the acid settles and may be drawn off through a 3- or 4-inch, lead-lined pipe that is welded to the bottom of the separator near the top of the plug. The sludge is next washed with water to remove more acid. These washings, thereafter, are passed to the acid vats. Washing of the sludge is continued until the average gravity of the acid in

the vats is such that further dilution would not be economical. Washing is never continued to such a point that the separated acid is lower in gravity than 30° Bé., and the gravity usually ranges from 33° to 35° Bé.

The separated weak acid obtained in the manner described is very dark in color and contains certain organic compounds resulting from the treatment of the oil. In this condition it contains only about 36 per cent. of actual sulphuric acid, water being present in the greater proportion. The amount of sulphuric acid recovered depends entirely on the nature of the sludge and the quantity of sulphonc acids which it contains. The results will vary with the grade of oil treated and the quantity and the density of the acid used for treatment. Light-oil sludge has been known to yield as high as 80 per cent. of the total acid originally present in the sludge, and lubricating-oil sludge, about 65 per cent.

36. In some cases, efficient recovery of acid from acid sludge, demands a process whereby it will be possible to heat the sludge to temperatures sufficiently high to effect rapid hydrolysis or a rapid splitting up of sulphuric-acid addition products by boiling with water to form sulphuric acid and neutral organic compounds, without permitting the escape of water vapor and the consequent loss of acid. This can be accomplished by heating under a slight pressure. The exact temperature, proper reaction time and dilution of the acid to be produced, in this method of hydrolyzation, will depend on the type and the properties of the sludges being treated. Thus, some naphtha sludges require only 1 hour's treatment at 275° F., producing 40° Bé. acid; cracked naphtha sludges require 1 hour at 320½ F., producing 45° Bé. acid; while a sludge produced in the treatment of kerosene with fuming acid at 150° F. requires 2 hours' time at 340° F. for hydrolysis, producing 49° to 50° Bé. acid. The pressures at which these operations are carried out vary from about 25 pounds per square inch for the naphtha sludge to as high as 65 pounds per square inch for the fuming-acid kerosene sludge. Operation of the sludge-treatment plant is continuous.

The retort used in this method of separating acid from acid sludge has a capacity of 100 to 125 tons of 40° Bé. acid. The retort consists of a steel shell approximately 30 feet long and 6 feet in diameter, lined with heavy sheet lead which, in turn, is overlaid with acid-proof brick set in acid-resisting cement. Such construction insulates the lead and protects it against corrosion and mechanical failure. Sludge, water and steam are intimately brought together in a mixing device, and are then passed into the retort or digester. The acid and tar separate into layers in the retort and may be withdrawn independently. Thus by suitable arrangement of the acid and tar outlets, any desired ratio of acid volume to tar volume may be maintained in the retort. The ratio of these constituents as they enter the digester is fixed by the composition of the sludge being retorted. If a mixture that results in the production of equal volumes of weak acid and tar is being charged in any batch process, the tar and acid both will be subjected to the same time-temperature treatment. On the other hand if, in the same case, the tar is withdrawn almost as fast as it separates, thus keeping a thin layer in the retort, the mixture will pass through the apparatus at a high rate. This is due to the fact that the mixture is subjected to the effect of the high retort temperature for a relatively short time only. The tar, therefore, will be less subject to oxidation. Consequently, it leaves the retort in a more fluid condition than otherwise would be possible. Another benefit derived is that the acid separates from a liquid tar more rapidly than from a viscous, stringy tar. By keeping the volume of tar in the retort reduced, the volume of acid which it is possible to carry in the apparatus is nearly doubled; as a result, the average through-put time of the acid is increased. This gives the mixture a relatively long digestion at high temperatures, a condition that is essential to the production of clean acid. Pressure retorting of sludge, in the experience of some refiners, almost doubles the yields of weak acid as compared with those formerly obtained. A further advantage claimed for the process is that, on account of the low carbonaceous content of the acid, subsequent concentrating difficulties have been largely overcome.

CONCENTRATION OF RECOVERED SULPHURIC ACID

37. General Practice.—In most refineries the weak acid coming from the separators at a density of about 30° Bé. is first concentrated either to 56° or to 61° Bé. The partly concentrated acid is then allowed to settle, so as to remove the tarry matter which has been separated by the decomposition of sulphonic acids during the first stage. The settled acid is then further concentrated in a second apparatus to a finished product of 66° Bé.

Many refineries use both 60° and 66° Bé. acid for treating oils. In such cases, it is more economical to concentrate to only 60° or 61° Bé., use a part of this acid for the treatment of light oils, and reinforce the balance to 66° Bé. by blending with fuming sulphuric acid which contains 20 per cent. free sulphur trioxide.

Where light oils and cracked distillates are treated with 60° acid only, it is possible to recover the acid in a simple and inexpensive apparatus. Even small refineries handling a few tons of acid per day can recover this acid economically. Refineries operating a contact sulphuric acid plant for the production of their make-up acid can recover the separated acid by concentrating to 61° Bé., and then using this acid in the absorbers of the acid plant where the weaker acid will be reinforced by sulphur trioxide either to 66° Bé. acid, 98 per cent. acid, or to 20 per cent. oleum or fuming sulphuric acid, as may be desired.

38. Simonson-Mantius Vacuum Process.—The Simonson-Mantius vacuum process consists in removing the water of dilution and concentrating the weak sulphuric acid to the desired density in a closed vessel under a relatively high vacuum by the application of indirect heat. High pressure steam or hot oil are most commonly used as the source of heat. The use of vacuum is especially applicable to the concentration of sulphuric acid, because distillation under vacuum reduces the boiling point of the acid to such a level that heating mediums of comparatively low pressure and temperature can be used. Thus the corrosive action of the acid is reduced and the con-

struction of the apparatus is greatly simplified. The difference in boiling points of sulphuric acid at various densities and pressures is illustrated by the fact that at a density of 30° Bé., the boiling point of the acid at 28 inches of vacuum is 120° F., as compared with 230° F. at atmospheric pressure, a reduction of 110° F. Under similar conditions, the reduction in boiling point for 61° acid is 150° F.; and for 66° acid, it is 180° F. These low temperatures make it possible to concentrate sulphuric acid to 61° Bé. with steam at 45 pounds pressure; and to 66° Bé., with hot oil at a temperature of 500° F. There is no difficulty in constructing extra-heavy lead coils to operate with a steam pressure of 45 pounds per square inch; and any high-grade lubricating oil with a flash point of 550° F., is suitable for the final concentration of the acid. This reduction in temperature reduces the wear on the apparatus, as chemical lead of good quality is not corroded by 61° Bé. sulphuric acid when the temperature does not exceed 300° F. In the Simonson-Mantius process the vacuum is created and maintained by special jet condensers, no vacuum pump being required. In this process, too, the acid is usually concentrated in two steps. This is done in order to permit settling of the acid at a density of about 60° Bé.

The weak acid is drawn by vacuum into the preliminary concentrator, which is heated by steam at 30 to 45 pounds pressure. As soon as a density of 56° to 61° Bé. has been reached, the vacuum of this unit is broken and the acid is discharged by gravity into a storage tank. The settled acid is again drawn by vacuum into the final concentrator, which is heated by hot oil circulated through an oil furnace of standard design. When the acid has reached a density of 66° Bé., the vacuum of this unit is broken and the acid is discharged by gravity into the cooler and the run-down tank. Where large quantities of acid are to be handled, it is possible to operate the concentrator continuously.

39. Advantages of the Simonson-Mantius Process.—In the concentration of sulphuric acid by the Simonson-Mantius process, the low boiling temperatures that prevail almost entirely

prevent the decomposition of acid. Further, no fumes can escape into the atmosphere, since any sulphur dioxide and sulphur trioxide fumes given off during the process of concentration are absorbed in the cooling water in the condensers. Because of the complete absence of all fumes, the concentrator can be placed where it is most convenient, that is, near the agitators or separating plant.

Because of the vacuum maintained in the whole system, acid leaks are impossible. Should any joint become defective, air will be drawn in and the vacuum gradually will go down. This gives the operator ample time to discharge the acid into storage tanks. Therefore, foundations and buildings cannot be damaged by acid escaping from the system.

The apparatus requires only a small floor space, about 1,000 square feet for a 20-ton plant, and about 1,500 square feet, for a 50-ton unit. The clearance between roof and ground floor is about 36 feet. Where climatic conditions permit, no housing is necessary for the concentrator. In any case, a plain building of structural steel with corrugated steel roof and siding is entirely satisfactory.

Since the acid is concentrated in a closed apparatus at reduced temperatures, the fuel consumption is quite low and the radiation losses are small. Depending on the density of the weak acid, the total fuel consumption varies from 50 to 70 gallons of fuel oil per ton of 66° acid produced. This amount can be reduced materially where exhaust steam is available for the preliminary concentration. Depending on the water temperature, the consumption of cooling water will vary from 20,000 to 30,000 gallons per ton of 66° acid. On account of its low acidity, the cooling water can be reused, if necessary. In such cases, however, about 10 per cent. of fresh water should be added daily. The total power consumption is from 20 to 25 kilowatt hours per ton of 66° acid. This includes the power required for pumping the cooling water. Repair costs are kept moderate by the careful selection of suitable material for the construction of the apparatus. The circulating oil is usually replaced about once or twice a year in order to give satisfactory results.

Vacuum evaporation greatly increases operating efficiency, as the boiling-points are lowered and radiation losses are reduced. On account of the low temperatures employed in the Simonson-Mantius process, very little acid is distilled over and, therefore, it is claimed that the total efficiency of the process is from 95 to 97 per cent. This refers only to the loss of sulphuric acid. There are no means of limiting the loss of sulphuric dioxide, which loss is due to the decomposition of the sulphonic acids. The amount of this loss depends entirely on the quality of the separated acid. Simonson-Mantius plants can be started in about 1 hour and can be shut down in about 20 minutes. This feature makes it possible to operate the concentrator intermittently, without appreciable losses and delay.

40. Chemico Process of Acid Concentration.—The Chemico process of sludge-acid concentration is based on the physical law that the boiling point of an acid of a given specific gravity is lowered when air is introduced directly into it. In the Chemico process, air at a temperature of 1,200° F. is blown through the acid bath, where it quickly gives up most of its heat and emerges at a temperature only a little above that of the acid itself. Thereafter, almost all of the heat remaining in the air is usefully employed in the preheating tower. The process is continuous, except that it is necessary to divide it into two stages in order to avoid the frothing and foaming due to decomposition of the hydrocarbons present. The two-stage concentration also makes it possible to remove most of the impurities in the first stage, partly by volatilization and partly by oxidation, so that a comparatively clean acid remains for concentration in the second stage.

Each Chemico type of acid-concentration plant includes two units, one for each stage. These units are almost identical in construction and are combined in one self-contained structure requiring a minimum of floor space. The sludge acid is contained in a rectangular lead pan, lined with acid-proof brick and carried on a raised concrete foundation. About two-thirds of the area of the pan is covered by an arch of acid-proof brick, through which enter the acid-proof iron pipes that discharge

the hot air beneath the surface of the bath. The air discharged through the acid bath is heated by the burning of oil in a combustion furnace of special design, which operates under pressure. A blower supplies the air under pressure, not only in the quantities required for the combustion process, but also a needed excess for regulating properly the temperature of the mass and for furnishing necessary oxygen to prevent dissociation. The hot air from the furnace passes through a header to the concentrator units, where the air is distributed through manifolds beneath the surface of the acid bath. In the rear of each pan is a preheating tower of acid-proof masonry packed with brick and furnishing the surface area necessary for the maximum absorption of heat from the escaping gases by the incoming acid. The usual acid air-lifts are used for pumping and regulating the acid supply, which enters at the top of the towers and flows downwards over and through the packing rings. The gases leaving the preheating towers are passed through Cottrell electrical precipitators to recover the acid present and to prevent fume nuisance.

In the operation of the Chemico process the rate of supply of acid to be heated is regulated to control the speed of concentration and the strength and temperature of the acid bath. In the first-stage operation, by regulating the temperature and quantity of air blown through the bath, the acid strength in the pan is maintained at 50° to 55° Bé., or just below the point at which foaming would occur. At this strength of acid, the hydrocarbons are largely broken down and volatilized by the rapid flow of hot air. The acid remains constantly at a strength sufficiently low so that the contained carbonaceous materials, tar, oil, etc., are not attacked. The acid from the first-stage operation drains off continuously and passes through a cooler into intermediate storage tanks, whence it is pumped to the top of the second-stage unit for final concentration. The preheated acid from the second or high-stage tower is maintained in the pan at 66° Bé. and is drawn off continuously at that strength. The finished acid leaves the concentrator at about 110° to 125° F., below its true boiling point. It is then used in treating oils and distillates in the refinery processes.

Consumption of fuel oil in the Chemico process is about 35 to 40 gallons per ton of 66° Bé. acid produced, when the process is started with 35° Bé. acid at room temperature. This is equivalent to about 9½ to 10 gallons of oil per ton of 66° Bé. acid when the process begins with acid of 60° Bé. strength. One man per shift is all that is needed to operate even the largest plant of this type.

41. Geyser-Action Process of Acid Concentration.—The apparatus required for the operation of the geyser-action process and the passage of acid through it, are shown in diagram in Fig. 2. In this process, hot gases from a suitable furnace *a* pass through a geyser flue *b*, which contains a pool *c* of the acid, that is being successively geysered up through the gas space above the pool. These gases act directly on the acid to which they are exposed in the surface of the pool, in the drops composing the geysers, and in the film of acid that is thrown on the ceiling and walls by the geysers. The geyser-action fountain is produced by discharging a stream of compressed air upwardly through the minute orifices in the nozzles *d* which are submerged slightly beneath the pool level, the air pressure and the submergence being adjusted to cause the geyser to rise to the height desired.

Since the flow of the acid is counter-current to that of the gases, which are drawn through the apparatus by the exhaustor *e*, the hottest gases meet the strongest acid; while the cold acid entering the other end of the flue meets the coolest gases. Evaporation of the water takes place, as a result of which the liquid body is reduced and concentrated. The gases entering the flue are added to by a large amount of water vapor and a small amount of acid vapor, and, at the same time, they are cooled greatly by the transfer of much of their heat to the liquid. As the gases, which are now growing cooler and cooler, approach the cold end of the geyser flue, they reach a point where the acid is no stronger than when it entered. However, the acid at this stage is at its boiling-point, having been preheated by the gases. In this preheating zone, the continuing loss of heat by the gases reduces their temperature to

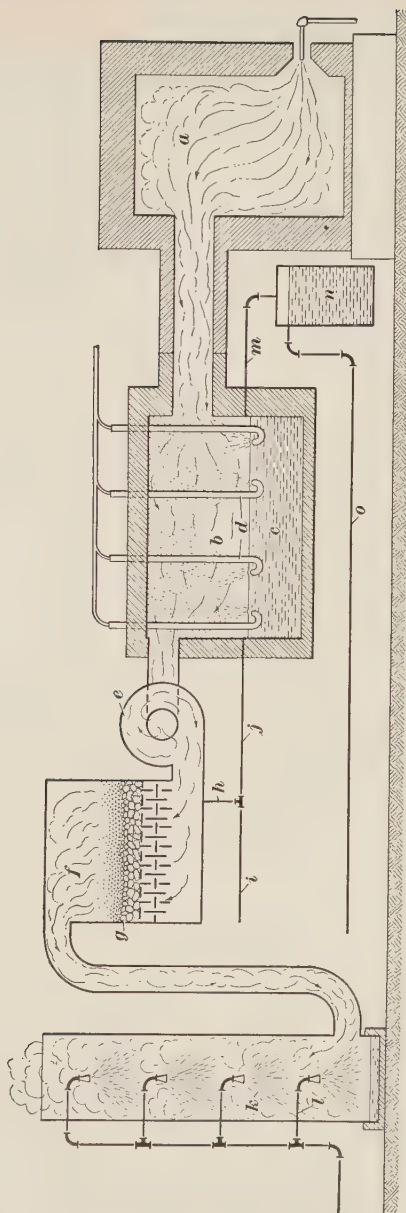


FIG. 2

a point below the boiling point of the acid vapors contained in them, thereby causing condensation of most of the acid vapors from vapor to liquid phase. This liquid is in the form of finely divided mist. The gases then consist of the furnace gases, together with water vapor and acid mist. These combined gases are now passed through a filter *f* which contains obstructions. The baffling material *g* within it so subdivides the gas passages that the gases flow through in many minute streams. These minute gas streams are continually impinging against the obstructions, thus filtering the gases by contacting the mist out of them.

The condensed acid or drip acid is returned to the geyser flue through the line *h*, which becomes part of the weak-acid feed line *i*. Almost all of the acid vapors are thus removed from the gases. However, in order to provide against the possibility of any objectionable quantity of such vapors being finally discharged to the atmosphere, the gases leaving the filter are passed through a condenser *k*. This condenser is simply a gas duct of enlarged area, in which the gas travel is slow, where successive sprays of water *l* are thrown against the gases in their passage through the duct. In reality, these sprays are atomizing sprays which deliver only a small quantity of water, but in such finely divided form that it is immediately absorbed by the gases. Such an arrangement causes the condensation and elimination of virtually all of the acid content of the gases before their final discharge to the atmosphere.

No provision for the removal of sulphur trioxide from the gases is needed. This is because no sulphur trioxide is formed, that is, no acid is actually split up. Splitting of the acid is avoided by not admitting the furnace gases to the strongest acid at too high a temperature. Also, by maintaining such an active flow of acid exposed to the gases at the pool surface, on the ceiling and walls, and in the geysered drops themselves, no portion of the acid in contact with the gases has its strength built up to the point at which sulphur trioxide would be split-off. The strong recovered acid, which is the product of the plant, passes through the line *m* into the receiver *n* from which it is pumped to storage through the line *o*.

42. Pan-and-Still System of Acid Concentration.—The pan-and-still system of sludge-acid concentration has been supplanted largely by the methods already described. This is because, in comparison with other processes, the fuel efficiency in the pan-and-still system is low, the labor costs are high, maintenance costs are excessive; the percentage of recovery of the acid is low, ranging from about 80 to 85 per cent., and, finally, obnoxious sulphur-trioxide fumes are given off.

In this system, lead pans, 12 to 14 inches in depth and eight or more in number, are arranged in series over flues that convey hot combustion gases from a coal- or oil-fired furnace. In evaporating 35° Bé. acid to acid of 66° strength, 50 to 65 square feet of evaporating surface for each ton of finished acid per 24 hours is generally required. Arrangement of the pans on the pan bench is such that the acid enters the first pan at the rear of the bench and then travels back and forth toward the combustion end. By the movement of the acid in this manner, the hotter flue gases are gradually encountered. Since the process is one of evaporation, and any scum that forms on the surface retards this action, all pans are made accessible for skimming. The building housing the pans is so constructed as to afford a natural circulation of air. This is done in an effort to increase the rate of evaporation and to reduce the fume nuisance within the building. In the pans it is practical to concentrate the acid to only about 60° Bé. strength because of loss of acid by evaporation. Further concentration to 66° Bé. is usually carried out in cast-iron acid stills, over which lead covers or domes are placed. These domes are fitted with lead troughs or flanges fastened to their exterior, over which cooling water is passed. Because of the obnoxious character of the vapors and the fact that the acid content of the fumes is now sufficient to make the condensate worth saving, the fumes leaving the dome of the still are condensed. In operation, two or more strong-acid stills are used in series. The acid flows from the last still to storage. It is a general practice to provide separate ovens for firing these stills. Ordinarily, the evaporating surface of such stills should be about 4 square feet per ton of 66° acid recovered per day.

HANDLING AND DISPOSAL OF ACID-FREE SLUDGE

43. After the acid has been separated from the acid sludge, the usual procedure consists in neutralizing the residual viscous sludge with either caustic-soda or soda-ash solution, and then mixing the neutralized sludge with fuel oil. This mixture is suitable for use as refinery fuel. In some refineries the sludge is never allowed to become cold after being drawn from the agitators, in which case it is burned without admixture with fuel oil. Almost all sludges except those from cylinder stocks can be neutralized and mixed with fuel oil without any difficulty whatsoever.

It is possible to remove a considerable amount of acid, remaining in the sludge after the separation of the major portion of the acid, by heating with live steam and blowing with air at the same time. Neutralization is accomplished by adding a solution of caustic soda or soda ash through a small line to the separator, and continuing the heating and the agitation. It is more economical to use soda ash than caustic soda, but there is greater danger that the contents of the kettle will boil over. Even with the use of caustic soda care must be taken that the sludge is not too hot when the soda is added, otherwise, the sludge may foam over the top of the kettle. As much as 10 barrels of 12° to 14° Bé. caustic-soda solution may be required to neutralize 100 barrels of acid sludge resulting from the treatment of pale or red oils. After the soda is added, the contents of the kettle are allowed to stand until the solution of caustic soda or soda ash has settled, this solution thereafter usually being discarded. The neutralized sludge is then either pumped to a tank where it may be mixed with fuel oil or it is mixed with the fuel oil in the separator. A half-and-half mixture is the ratio usually maintained between the sludge and fuel oil.

Little difficulty is encountered in handling sludges resulting from the treatment of pale and red oils, but considerable difficulty is often met with in disposing of cylinder-stock sludges. This is because of the nature of the sludge itself, as it is a very heavy, viscous material when hot, and almost coke-

like in its appearance when cold. In this case the ordinary equipment usually available for the disposal of sludge is not satisfactory, and a slightly different procedure must be followed. In refineries where heavy cylinder-stock sludge is not mixed with fuel oil, its disposal becomes a serious and costly operation. At some refineries monorail cars transfer the sludge to the boiler house, where it is burned merely as a method of disposal and with no thought of any fuel efficiency. The acid remaining in the sludge attacks everything with which it comes in contact, and for this reason the cost of repairs is exceedingly high. This procedure is only followed where no land is available for storing the sludge. Other refiners haul the sludge from the agitators to a suitable dumping ground where the sludge is piled up year after year. Such a procedure frequently brings complaints from surrounding farmers, whose crops are injured by the acid which the rains wash from the sludge onto their soil.

Some refiners take advantage of the fact that, if the sludge as it comes from the separators is washed with cold water, it becomes granular and coke-like in nature. Washing with cold water is effected by having the sludge propelled up an inclined trough by a spiral conveyer while water is sprayed over the length of the trough. This water then drains to sewers located at the lower end of the trough. The coked mass is delivered at the high end of the trough ready for disposal. If properly handled, the resulting coke may be mixed with coal and burned.

FILTRATION OF LUBRICATING OILS

44. Purpose of Filtration.—Many lubricating oils reach the market following a chemical treatment, but most motor oils and the better grades of engine and machine oils are in addition filtered through adsorbents before the products are considered to be sufficiently refined. However, many lubricating oils made from the paraffin-base crudes of Pennsylvania, are purified by filtration alone, chemical treatment not being required.

Generally speaking, it may be said that the purpose of filtration of oils is to make them more valuable, either by increasing their useful qualities or by making them easier to market,

Specifically, adsorbents decolorize an oil by removing solid suspended matter, and colloidal and dissolved impurities, such as small particles of coke, finely-divided and colloidal carbon, complex tarry compounds of high molecular weight, dissolved coloring matter, as well as traces of suspended alkali, acid, and moisture. Practically, color has little bearing on the lubricating qualities of an oil. However, a light, clear color is at least a good selling point, since the oil looks pretty and inviting. Good color indicates, by inference, that the oil has been carefully refined and handled throughout, whereas poor color may indicate the presence of impurities.

45. Adsorbent Materials.—For the filtration of lubricating oils, fullers' earth continues to be the most widely used of all adsorbents. Fullers' earth obtained its name from the fact that it was first used for fulling, or removing grease from woolen goods. This substance is commonly called a clay, although in reality it is a clay-like mineral that contains a relatively high percentage of aluminum silicate. Approximately 93 per cent. of the fullers' earth mined in this country is obtained from Georgia, Florida, and Texas. The bleaching or decolorizing value of fullers' earth is dependent almost solely on its physical structure, which may be imagined as being porous, like a sponge, and it possesses the ability to take-up or adsorb so-called impurities. A chemical analysis is not indicative of the value of the earth, or clay, as a decolorizing agent, and the extent to which it will remove color from an oil can be determined only by actually filtering oil through the earth in the laboratory. Clay minerals of the bentonite type after being treated by acids are very efficient decolorizing agents. Such acid-treated clays are being used extensively in the contact filtration of lubricating oils. Bone black is seldom used at the present time as a medium for the filtration of petroleum products.

46. Methods of Filtration.—Lubricating oils are treated with adsorbing substances by filtration through a column of coarsely ground fullers' earth, the process being known as percolation filtration; or by the so-called contact process of filtration.

Any desired degree of refinement can be obtained by either the contact or the percolation filtration methods, and the choice between them depends only on practical conditions. The thing to be considered is whether the whole filter product is desired in one particular quality, or whether it is advisable to have such product divided into several fractions of various degrees of refinement. In the first case, contact filtration probably would be more suitable; in the second, the percolation method.

47. Percolation Filtration.—For the percolation method of filtration, fullers' earth of the following grades are commonly made: 16 to 30 mesh, 30 to 60 mesh, and 60 to 90 mesh.

The mesh, or fineness, of earth that it is most advantageous to use depends largely on the characteristics of the oil being filtered. Coarse clays are preferable for the more viscous oils. Earths of finer mesh can be used satisfactorily on oils of lighter body. The finer the earth, the higher is its efficiency as a decolorizing agent; but the slower, with oils of the same viscosity, is the rate of filtration. Experience has shown that 30 to 60 mesh earth is approximately 20 per cent. more efficient than the 16 to 30 mesh product; and the 60 to 90 mesh earth, from 10 to 15 per cent. more efficient than earth of 30 to 60-mesh fineness. Ordinarily, neutral oils and cylinder stocks in solution should be filtered through 60 to 90 mesh earth, and steam-refined and bright stocks, petrolatum and wax, through the 30- to 60-mesh grade of earth. Practical conditions largely influence the mesh of earth, or clay, to be used.

48. Filters.—In decolorizing by percolation, refiners most frequently use a vertical type of filter, provided at the bottom with a blanket-covered, perforated drainage plate to hold the clay, or earth, and equipped with manholes at the top and at one side near the bottom for charging and discharging the clay. The filters vary from 6 to 10 feet in diameter and from 14 to 30 feet in depth. The depth must be such that the clay and oil will be in contact for such a length of time as will result in the removal of a maximum amount of color from the oil. However, if the filters are made too deep, there is the increased danger of channeling of the oil to be considered. Channel-

ing is the term applied to the action that occasionally occurs when the oil passes directly down through the filter following isolated paths and thus not coming into intimate contact with all of the clay, that is, without being absorbed by the clay.

The rate of flow of oil from a filter is dependent on the diameter. Filters should be designed for a pressure of from 40 to 50 pounds per square inch. It has been found that spent clay in a filter has an angle of repose of 40 degrees from the horizontal. Filters are therefore designed either with cone bottoms, usually on a 45-degree slope, as a result of which they are virtually self-dumping, or with the dished-type of bottom, the advantage of which is the absence of seams.

Various means are employed to hold the clay in the filter and to prevent it from coming through into the filtrate. The usual method is to place a canvas blanket over the bottom, and this blanket is sometimes supported on a perforated screen, while in other cases, it lies directly upon the bottom. Difficulty in holding back the clay is frequently experienced at points where the blankets join the steel shell of the filter and at the necessary opening for discharge of the spent clay. To overcome such trouble, devices ranging from complicated metal attachments to the insertion of old burlap bags in the bottom of the filter have been used. None of such means is entirely satisfactory; for sooner or later, the canvas becomes rotted and frayed and must be replaced. When the blanket is changed, the filter is out of service for a period of from one to three days, depending on the degree of simplicity of its fastening.

A device that has been found efficient for retaining the clay is shown in Fig. 3, in which the outside of the filter *a* is shown in view (*a*) and the inner construction in view (*b*), which is partly in section. The device comprises a screen *b* to retain the filtering medium, a clay gate *c*, and a manhead cover *d* all in one. When a filter equipped in this manner has been filled with clay, the gate and the manhead cover are closed. The clay fills the neck inside of the screen and cannot get past the metal sealing-rings *e* into the annular space around the screen. In operation, after the filtered oil has passed through the screen, a pipe *f* tapped into the neck conveys the oil to the run-down

tanks. To dump the filter, the cover is swung back on its hinges and the clay gate is opened to allow the clay to run out. The screen is made of heavy, monel-metal cloth, which will give several years of wear. When it is necessary to remove this cloth, a new one can be inserted in a few moments.

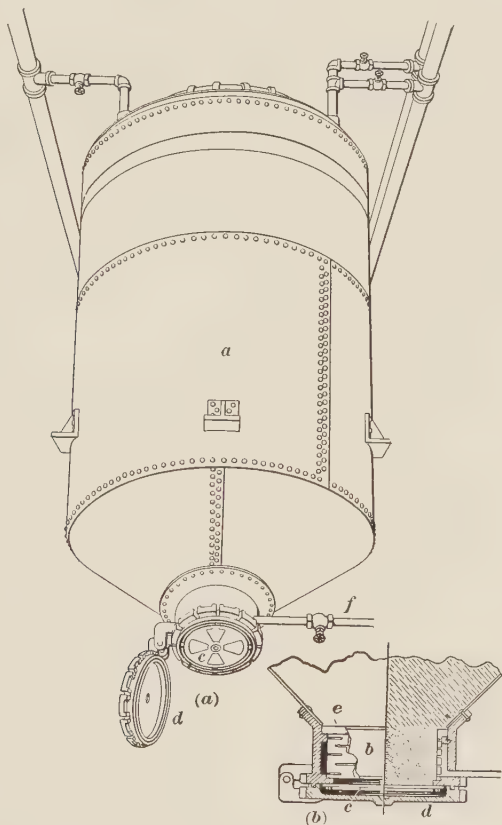


FIG. 3

49. Tempering of Fullers' Earth.—Most fullers' earths attain their highest adsorptive efficiency after a slight burning, during which not only hygroscopic water but also part of the water of composition is driven off. This heat treatment is called the tempering of the earth. Too strong a burning tends to fuse and to close the pores of the clay, thus lessening its

decolorizing value. Coarse-mesh earths are usually tempered by heating to temperatures ranging, approximately, from 500° to 800° F. Clays from various regions require different temperatures for bringing them to their maximum efficiency. Whereas, formerly, less dependence was placed by refiners on the temperatures attained in tempering than on the color of the earth, the tendency now is to watch closely the temperature of burning by the use of suitable pyrometers.

50. Packing the Filter.—In charging filters, best results are obtained if the earth is leveled off and tamped at least three times while the clay is being put into the filter. Such procedure will tend to prevent channeling of the oil. Leveling off and tamping keeps the whole charge of earth homogeneous and prevents the larger grains from rolling to the sides of the filter, under which condition a core of fine earth exists in the center of the filter. In a filter that has been improperly charged, the coarse earth next to the sides of the filter will soak up oil quickly, whereas the fine earth in the center will absorb oil only very slowly. Consequently, in the filtration process, the oil in a filter thus packed will travel toward the sides and will percolate through the coarse earth, while little or none will filter through the closely packed earth in the center. Since under such a condition there may be several tons of earth in the filter that are not performing any filtering function, it is obvious that a filter so charged cannot give the yield per ton that it should. Further, such a filter is very difficult to drain, wash, and steam, and the spent earth discharged from it causes more trouble in subsequent reburning than does clay from a properly packed filter. Other precautionary measures to be followed in reducing the tendency of oil to channel include either the insulation of the outside of the filter or locating the filter in a compartment where the temperature of the earth and of the oil will remain almost constant throughout the entire run.

51. Filtration of Oil.—The temperature at which oils are filtered varies with the viscosity of the oil. Undiluted cylinder stocks require the highest temperature, and for best results this

temperature should not be over 150° F., although some refiners still filter at temperatures around 160° to 170° F. More often, however, cylinder stocks are filtered mixed with about an equal volume of naphtha at a temperature of about 125° F. Neutral oils should be filtered at a temperature of not over 100° F.; and waxes and petrolatums, at a temperature of about 25° F., above their melting points.

Filtration may take place either with gravity or pressure feed, although the latter method seems to be preferred. After the filter has been charged with clay, the manhead cover at the top of the filter is closed. The oil to be purified is then pumped in through a line at the top of the filter, under a pressure of about 5 pounds per square inch, until the oil begins to come through the clay. The pressure is then increased to about 15 pounds per square inch. The first of the oil to come through is light in color, gradually getting darker as filtration proceeds. Pumping of the oil through the filter is continued until the blended filtrate in the receiver reaches a color standard previously established. Both the oil pressure on the filter and the rate of flow should be constant for the entire run. The rate of flow can be made constant by running the oil stream through the particular size of hole in the line that will secure the desired flow. It is good practice to have installed in the line, at some point between each filter and either the common tank or the manifold leading into the tank, a device that will control and keep uniform the speed at which the filter is running.

One filtration is sufficient for neutral oils, waxes and petrolatums when filtered to the usual colors. Cylinder stock, either undiluted or in naphtha solution, generally requires several filtrations. The unfiltered cylinder stock is first passed through a filter containing clay that has very little decolorizing value. The effluent from this filter may then be directed to two or more filters, the filtered oil from which has reached the point where it has become off-color. It is from these filters that the filtrate is secured to soak up newly charged filters and to supply filters the oil from which is of the proper color. By means of a closed system this may all be done with the original pumping, starting at 35 to 45 pounds pressure per square inch; the oil then passes

through the filters and heaters in the required order. By such an arrangement, contact of the oil with the air is avoided. Oil thus handled, filters with the greatest facility.

52. Draining, Washing, and Steaming of Filters.—After the fullers' earth has adsorbed coloring matter and other impurities to the limit of its capacity, filtration is stopped and the filter allowed to drain. Draining is generally accelerated by the use of air pressure or steam. The use of steam both aids in draining and in removing the slime that is deleterious to efficient filtering. Light naphtha is then pumped through the filters, 6 or 7 barrels of naphtha being used for each ton of clay. Naphtha of 52° to 56° A. P. I., or even higher, is desirable for best and most economical results in washing. After the clay and naphtha have soaked for several hours at a temperature of about 150° F., steam is introduced into the filter to displace both the naphtha and the oil that has been washed from the clay by the naphtha. If deemed advisable, the washings are repeated until the color of the naphtha used for this purpose shows that all naphtha-soluble oil has been removed from the clay. The clay in the filter is then steamed at a pressure of about 40 to 45 pounds per square inch, the operation being continued until the clay is free from naphtha. That this point has been reached is indicated when the condensate shows the presence of no oil and the clay is thoroughly dry. This operation requires approximately 15 to 18 hours for completion. During the steaming operation, it is advisable to close partly the outlet of the filter to make reasonably certain that the steam is reaching all of the earth. When the clay is dry, the pressure is released and the manhead cover removed to cool and dry. The oil and naphtha are recovered from the washings by distillation.

53. Classification and Revivification of Clays.—Clays or fullers' earths are usually classified by numbers that indicate successive revivifications. Thus No. 1 clay, in addition to the original tempering, has been burned once, No. 2 clay, twice, etc. Another system that has the advantage of giving a symbol to the clay at each separate stage of its life is as follows:

	CLAY NUMBER
New clay	0
New clay, dehydrated or tempered.....	$\frac{1}{2}$
New clay, dehydrated and used once.....	1
Clay, after one revivification	$1\frac{1}{2}$
Clay, used twice	2
Clay, after a second revivification.....	$2\frac{1}{2}$

For purposes of economy fullers' earth is revived by burning and is then reused. Revivification is accomplished by transferring the dry, used clay, by suitable mechanical means, from the filters to kilns of a suitable type, where the tarry coloring matter is burned out of the pores of the clay by heating to a temperature sufficient to secure this result, but not high enough to disintegrate the clay. Temperatures of burning vary from 600° to 1,000° F. The use of pyrometers is essential for maintaining correct temperatures.

54. Revivification Kilns and Furnaces.—Early practice favored the use of the rotary kiln for reburning clay, and many of them are still used by refiners. The rotary kiln consists essentially of an inclined steel shell, lined with firebrick or other refractory material and mounted on rollers in such a manner that the whole is made to revolve by a train of gears. The spent clay enters at the rear or high end of the kiln and discharges through the bottom of a movable housing which is placed at the low or front end of the kiln. Burners are introduced through the housing. The products of combustion leave the kiln through the rear stationary housing and stack. In order to cool the clay for safe and convenient handling, it is delivered from the kiln to a rotary cooler that is placed beneath it and supplied with draft by a separate stack. In this manner the earth is brought to a temperature of 130° to 150° F. Fuel consumption of rotary kilns is from 10 to 12 gallons of fuel oil per ton of clay burned.

55. Because of their greater efficiencies, multiple-hearth roasting furnaces are gradually replacing the older types of equipment used for revivifying fullers' earth. The purpose of

any revivification furnace is to dry out the moisture, burn off the oil, and remove the accumulated carbon from the grains of the earth. The older-type horizontal, vertical, and rotary burners, in which the time element and the amount of oxygen present could not be properly controlled, could not affect this carbon, but instead tended to bake it into the clay. With the multiple-hearth furnace, on the other hand, there is the right amount of exposure of all of the earth to the heat over a controllable time period. Further, the oxygen in the introduced air unites with the carbon on the earth, resulting in the combustion of the carbon. The temperatures in the multiple-hearth furnace are lower than in the old-type furnaces, thus preventing the small amount of vitrification of the grains that was formerly experienced. By the use of the multiple-hearth furnace it is now possible to retain earth in service indefinitely at around 80 per cent. of its original efficiency, when about 3 per cent. of new earth is added after each burning to make up for losses in handling.

56. Contact Filtration.—The contact-filtration method of purifying oils with adsorbent materials has been supplanting the percolation method. Contact filtering of oils consists of mixing, with the aid of heat, a finely divided adsorbent clay with the oil and subsequently removing the clay by the use of suitable filter presses. The basic principle of this process hinges on the fact that the rate of decolorization is dependent on the fineness of the adsorbent medium. Therefore, since clays of 100 to 200-mesh fineness present more surface to the oil than a 16 to 30, 30 to 60 or other coarse-mesh product, a maximum decolorizing effect is obtained in a minimum of time by the use of such finely divided materials.

In the process of filtration by contact one or more tanks must be provided in which the clay and oil can be mixed. Such tanks preferably should have a conical bottom and closed top, but should have a vent through which steam or other gas can readily pass off. The tank or tanks must be provided with some means for violently agitating their contents, since the efficiency of the fine clay depends on intimate and thorough con-

tact with the oil. Air agitation is not recommended, since this introduces the possibility of oxidation of the oil, particularly at high temperatures. Mechanical agitators of the propeller type are satisfactory, but recent results with agitation by circulation have indicated that this method is more economical and possibly more efficient. In the process, the oil is drawn out of the mixing tank by a low-head, high-capacity, centrifugal pump and discharged back into the tank through a line entering the tank at a tangent on its vertical side above the cone. A pump with a capacity sufficient to turn over the contents of the tank every three or four minutes is recommended. Such an arrangement keeps the material in the tank in violent motion and, at the same time, is continually insuring very thorough mixing of oil and clay in the pump. If the mixture is to be heated to a high temperature, as is customary in treating lubricating oils, it is well to insulate the tank, and, of course, some arrangement for heating is necessary.

57. Heating Units.—The type of heating unit used depends on the amount of oil to be handled and the temperature to which it is to be heated. If the temperature is to be 250° F., or less, steam is usually the source of heat and is applied by means of closed coils within the tank or through an ordinary steam jacket. Where the circulation method of agitation is used, the steam heater very well can be in the form of a heat exchanger inserted in the circulating line. Where temperatures of 250° to 450° F., or higher, are used, a direct-fired pipe still is undoubtedly the most economical method for heating the clay-and-oil mixture. The heating unit used, regardless of type, should have sufficient heating capacity so that the rest of the plant at no time will be delayed by having to wait for the heater to get the mixture up to the proper temperature.

58. Operating Procedure.—In decolorizing and otherwise purifying oils made from either mixed or asphalt-base crude oils, the major portion of the work is accomplished by treating the oil with sulphuric acid, because sulphuric acid, in proportion to the amount of purification effected, is far cheaper than any known adsorptive material. In many instances, however,

decolorization to the preferred point by the use of acid alone is either impossible or does not produce oils of the most desirable characteristics. In determining the method of utilizing the process of contact filtration, in connection with the finishing of oils of this character, it is most essential that the acid treatment of the oil and the subsequent clay treatment be balanced one against the other in order to get the best as well as the most economical results. In some instances, the desired color of the oil is obtained almost entirely by the use of acid alone, in which case the clay is utilized as a neutralizing agent and for the purpose of stabilizing the color of the final product. In other cases, acid-sludge losses are so high as to prohibit too great a reduction in color by an extensive acid treatment, wherefore clay is employed in more abundant quantities. In the majority of instances where oils are treated with acid, the clay is added to the acid oil which has not previously been neutralized. The clay then acts both as a neutralizing agent and a decolorant. Higher efficiencies are obtained from clay applied to oil in the acid condition. In a few cases, prior neutralization of the acid oil gives a greater efficiency, but even in such instances the neutralization is not carried out to completion; consequently, the oil is still slightly acid at the time the clay is added to it.

From the acid-treating agitators the acid oil is pumped to open-top, conical-bottom mixing tanks, where from $\frac{1}{4}$ to $1\frac{1}{2}$ pounds per gallon of 100 or 200-mesh clay is added to the oil and the whole either mechanically agitated, or circulated by pumping from the bottom to the top, or both means may be utilized. The quantity of clay used is dependent on the nature of the oil and the extent to which it is to be decolorized. Because the entire aim of the process of contact filtration is to bring the adsorptive material into intimate contact with the impurities in the oil so that they will be absorbed by the clay, in almost all instances the efficiency of any adsorptive material will depend largely on the temperature to which the oil is heated after the clay has been mixed with it; for, the higher the temperature, the less viscous the oil, the more intimate the contact and, therefore, the better the result. With most filtering materials, the clay will reach its greatest efficiency when the oil has been

brought to a temperature sufficiently high to start decomposition of the oil itself. In operation of the process, the oil is heated, either in a steam-heated mixing tank or by being circulated through a direct-fired pipe still, to the temperature at which a practical maximum decolorizing and deacidifying efficiency will be obtained from the adsorbent. Ordinarily, these temperatures vary from 250° to 450° F. While, as already mentioned, the higher temperatures tend toward more efficacious results, the advantages therein are counterbalanced somewhat by the tendency of the oil at such temperatures to oxidize and, hence, to darken more quickly. An improvement in the process involves the maintenance of a slight pressure on the system during the heating of the oil and clay mixture to the temperature at which maximum decolorization is obtained. After the clay and the oil are mixed and brought to the desired temperature, the hot oil is cooled and the spent clay is removed by filter pressing. When the press becomes filled with spent clay, the resulting cake is blown with air or high-pressure gas as a means of reducing to a minimum the amount of oil retained by the cake. The filtering operation is carried on most frequently at a fairly-high temperature. However, when a residuum requiring subsequent dewaxing has been clay-treated, inasmuch as the oil requires dilution with naphtha to prepare it for the dewaxing operation, the oil is diluted before the removal of the spent clay, and the pressing operation is then carried on at a normal temperature.

59. Filter-Press Operation.—Numerous types of presses for separating the clay from the oil have been and are being used by refiners, but the Sweetland filter press, which is of the pressure-leaf type, is now most widely employed in contact-filtration plants. In filtering materials at temperatures below 200° F., where acid or alkali is not present in the oil in appreciable quantities, a special cotton filter cloth can be used as a filter medium with good results. When oil is to be filtered at temperatures above 200° F., the use of monel-metal filter cloth is recommended. This filter screen is both acid- and alkali-proof and heat-resisting.

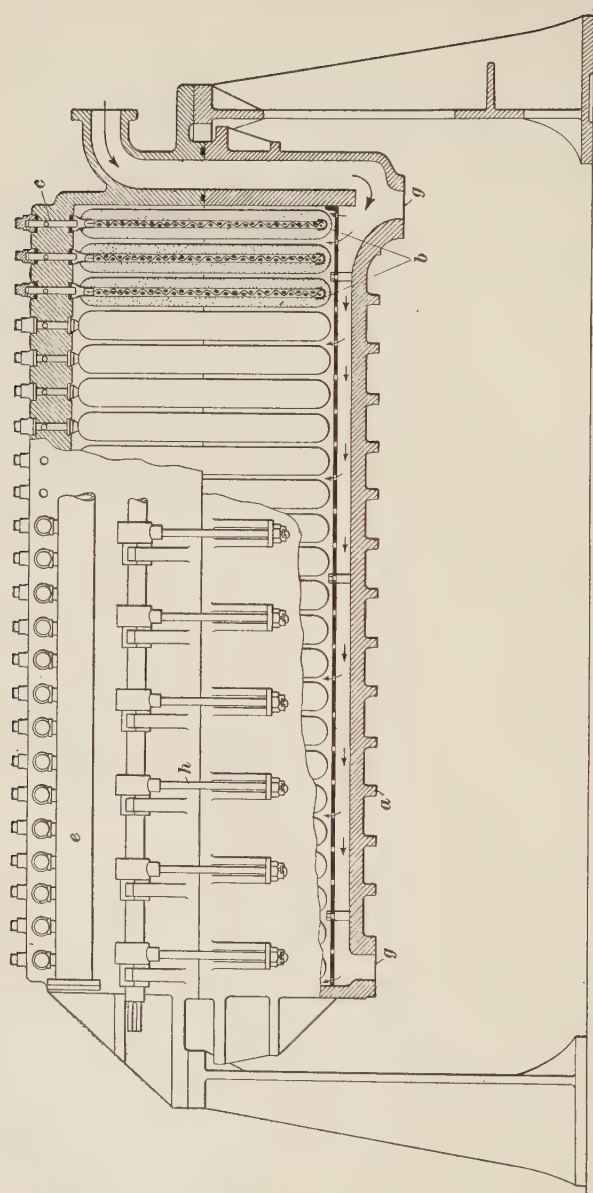


FIG. 4

The operation of the filter press is illustrated in Fig. 4, which is a side view of the press with part of the outside shell broken away to show the construction, and in Fig. 5, which is a cross-section at one of the leaves. Like parts are lettered alike in both views. In starting up, the first step consists in filling the filter body or shell *a*, with the mixture to be filtered, the air in the body being allowed to escape through a convenient vent while filling. The oil is forced into the filter, usually at a pressure of about 40 pounds per square inch, by means of a

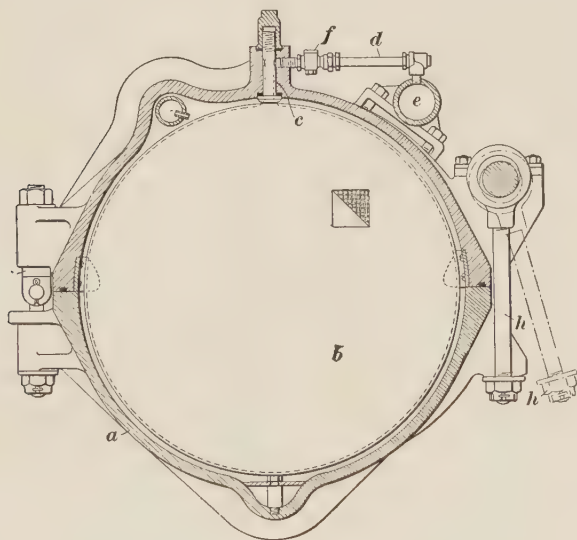


FIG. 5

pump. When the filter body is full, the air vent is closed. Since there is no exit from the filter body, other than through the filter cloth on the leaves *b*, the pressure forces the clear oil through the cloth to the interior of the filter leaves, the heavy wire screen inside the cloth envelope or bag furnishing ample drainage for the filtrate, and by reason of the pressure in the filter body, the clear oil passes out of the leaf, through the filter-leaf nipple *c*, the sight glass *d* and into the filtrate delivery pipe, or manifold *e*, to which all leaves are connected. The sight glasses consist of heavy, glass tubing which gives the operator

in charge a clear view of the flow from each filter leaf. If, for any reason, the cloth on any leaf has been torn or is worn out, and the filtrate is not clear, a shut-off valve *f* may be closed and the defective leaf shut off from further filtration until the filter is discharged, at which time the leaky leaf is removed and a spare one inserted.

The first oil through the leaves may contain some clay, but the cakes begin to form immediately, and within a minute or two all streams are clear. The cloudy oil that first comes through is by-passed back to the mixing or contact tank, but as soon as the sight glasses are all clear, the filtrate is sent to the finished-oil tank.

The filtering rate at the start is four or five times the average rate; hence it is essential that a pump of sufficient capacity be used to take advantage of this high initial rate. As filtration proceeds, the suspended earth or clay accumulates on the surface of the filter leaves, forming the cake, the average thickness of which in this kind of work is 1 inch. The increasing cake thickness during the filtering period causes the rate of filtration to slow down and it is then usually necessary to by-pass some oil from the filter shell in order to hold the pressure down to 50 pounds and to assist in keeping the clay in suspension within the filter shell. After sufficient oil has been pumped to the filter to give a 1-inch cake, filtering should be stopped. The operator knows when the filter cakes have been built up to the proper thickness by timing the filtering operation. In other words, he knows by experience how many minutes are required to form a cake of the proper thickness. In some cases a measured quantity of the oil is pumped in for each charge as a means of controlling the cake thickness, and in others the amount of filtrate produced is used as an indication.

Before the feed pump is stopped, air is turned into the filter so that a positive pressure will be maintained and the cakes held in place on the leaves. As soon as the pump is off and a steady air pressure is obtained, the drain valve *g*, Fig. 4, on the lower shell is opened and the excess oil is blown back to the contact tank. Air pressure of 30 to 50 pounds is maintained on the filter shell. The air passing through the cakes drives out the

oil and dries the clay. As soon as the sight glasses show very little oil coming through, the air is turned off and the pressure on the shell is released.

The method of discharging the filter is simple and involves little labor. When the cake has become of fair thickness and weight, the bolts *h*, Figs. 4 and 5, are loosened and the filter is swung open on the hinges *j*. Then the current through the filter leaves is reversed, that is, air is turned into the filter leaves, which slightly inflates the cloth, dislodges the cake, and causes it to fall into a car or conveyer underneath the filter. Not only does this operation discharge the filter, but the air passing through the pores of the cloth opens them and puts the cloth in good condition for further filtration. The time required for discharging varies with the size of the filter and the nature of the material. Some of the larger filter presses that dump 55 cubic feet of cake at a charge require only 5 minutes to open, dump and close, after which they are ready for the next charge.

60. Clay-Pulp Contact-Filtration Process.—The clay-pulp contact-filtration process of purifying oils differs from the process previously described in that the adsorbent is applied to the oil in the form of a clay pulp containing about 30 per cent. of solids. The adsorbent is a clay of the bentonite type that has been treated with from 40 to 50 per cent. of its weight of sulphuric acid. The resulting product is then washed free of reaction products and allowed to settle to the consistency of a slimy mass or pulp. The process is especially applicable to the filtration of residual oils, such as long residuum and steam-refined stock from which bright stocks of various specifications are manufactured. The advantage of the method lies in the fact that the particular clay used, after acid treatment, when applied to the oil in the form of a clay pulp, is from four to ten times more efficient than an equal weight of any known finely divided clay of from 100 to 200-mesh fineness when applied to the oil in a dry state.

The procedure involved in the preparation of the treated clay pulp consists essentially in grinding and pulverizing the crude clay so that at least 85 per cent. of it is of 200-mesh fine-

ness. From the pulverizer the ground clay passes to a ground-clay bin. In the meantime, the required amount of 66° Bé. sulphuric acid and water has been mixed in a lead-lined cooker. The acid solution contains 20 per cent. by weight of sulphuric acid. From .4 to .5 of a pound of 66° sulphuric acid per pound of dry clay to be treated is a suitable quantity. The exact amount of acid to be used depends on the increase in the adsorptive efficiency of the clay with an increase in the amount of acid used. In other words, there is an economical point at which it is not advisable to use more acid in treating the clay.

When the acid solution has been brought to the required 20 per cent. strength, and the proper amount of acid is in the cooker for the treatment of a given quantity of clay, the desired amount of ground clay is automatically weighed and transferred into the clay cooker. A splash plate near the top of the cooker serves to distribute the clay over the surface of the acid mixture and thus prevents the formation of lumps. Air under sufficient pressure to overcome the hydraulic head is admitted through the cone of the cooker, and the mass is kept agitated during the addition of the powdered clay and for some time thereafter. When the clay has been thoroughly mixed with the acid, exhaust steam is admitted to the jacket and to the space below the cone of the cooker. The batch is agitated at intervals to keep the clay in suspension during the early part of the cooking operation. After 4 to 6 hours, most of the acid solution has been adsorbed by the clay, and a pulp formed that does not require further agitation. The cooking is usually complete in 6 to 8 hours, but to prevent irregularity in quality it is desirable to allow the batch to stand for 18 to 24 hours. At the end of that period of time the cooker is filled with water, the mass being agitated during the addition, after which the whole is pumped to a water-wash tank, allowed to settle, and the supernatant liquid is pumped off and wasted. The treated clay is then washed with water at a temperature of about 180° F., allowed to settle and the supernatant liquid is pumped off, the process being repeated until the acidity of the mass has been reduced to a minimum. On completion of the last wash, the clay is allowed to settle until it is as thick as can be handled

readily by a pump, this thickness corresponding to a pulp that contains about 30 per cent. of solids. The clear water, then, is pumped off as completely as possible, and the remaining pulp is pumped to the pulp-storage tank, from which it is drawn when needed for use in the process.

61. The equipment required and the operating procedure followed in the clay-pulp process are similar to those of the dry-clay, contact-filtering method. By previous laboratory experiment, the quantity of clay pulp required to give the necessary bleach to the quantity of oil to be treated is ascertained. By means of separate pumps, the proper amounts of pulp and of oil are delivered to an emulsion tank equipped for mechanical agitation, and after agitation, into a heating element such as a pipe still, in which the mixture of clay pulp and oil is raised to a temperature at which both the water will be driven off and the maximum decolorizing and deacidifying efficiency will be obtained from the clay. The temperature at which the clay shows its greatest efficiency is usually that at which there first takes place a slight decomposition of the oil. The mixture of oil and clay left after the water has been driven off is discharged into a so-called oil or vapor separator, and therein thoroughly steamed to remove the lighter vapors. It is usually desirable to have the vapors coming off from this separator pass to a suitable water-cooled condenser. The steamed mixture of clay and oil is then filtered to remove the spent clay. Any suitable type of filter press may be used. The filtered oil passes through cooling coils, thence to a small run-down tank and thereafter to storage.

62. Combined Contact Filtration and Distillation.—One of the most interesting developments in connection with the process of contact filtering has been that in which the clay is applied to the oil during the process of distillation. The procedure with dewaxed crude oils consists essentially in the distillation of the crude oil by its continuous circulation from a separator tank through the coil of a pipe heater and back into the separator tank again. Circulation in this manner is continued until the

crude is reduced to the required specification. Dry clay is then mixed into a paste with oil that has been previously filtered, sufficient oil being used in making the paste to permit the pumping of the mixture. When the temperature of the oil being distilled reaches 350° F., the oil and clay paste containing sufficient clay to give the desired color-reaction to the ultimate residuum is pumped into the feed line leading to the coil of the heater. The clay-oil paste is added slowly so that, by the time the oil has been reduced to specification, the entire charge of clay has been incorporated with the oil, which has then been efficiently decolorized. When the oil has been reduced to the desired point, the clay-charged oil is then pumped from the separator tank, cooled and the clay removed by filter-pressing.

The process may also be satisfactorily used in connection with the filtration of overhead stocks, in which the oil is being reduced to final specification after initial distillation; for the filtration of oils that have been diluted prior to acid treatment, in which case the clay may be applied to the oil at the same time that the diluent is being distilled off; and in the filtration of residuums made from mixed-base crudes, wherein the crude itself has been acid-treated, neutralized and the clay introduced during the process of reducing the treated crude.

63. Advantages and Disadvantages of Contact Filtration.

In the contact filtration of oils, time is saved over percolation filtration methods, due to the greater speed in obtaining the same decolorizing results. Also, this process renders possible the use of acid-treated clays which, weight for weight, are much more efficient than fullers' earth. For practical reasons, such treated clays cannot be used in a coarse state. The initial costs for the construction of a plant are less, in the case of the contact filtration process, than in the percolation process. An outstanding disadvantage is that no suitable means has been devised for revivifying the spent, finely divided clay. Recent investigations, however, indicate that the multiple-hearth furnace, fitted with a dust-collecting system, eventually will solve this problem.

WAX-PLANT CONSTRUCTION AND OPERATION

64. Introductory.—Paraffin wax is solid at ordinary temperatures. Therefore, the presence of wax in an oil raises the temperature at which such oil will flow. Hence it is necessary to remove most of the paraffin wax contained in an oil before the oil becomes a marketable product. As already mentioned, the wax-distillate cut from the crude oil is the source of lubricating oils of lighter body. Wax distillate is obtained only from paraffin-base or mixed-base crude oils and not from asphalt-base crudes. Due to the presence of the wax, wax-distillate is semisolid at temperatures ranging from 60° to 65° F. If this distillate is cooled to 20° F., it becomes a solid with a consistency similar to that of a grease. The first step, therefore, in the removal of wax is to cool the wax-bearing distillate. This is done by mechanically forcing the distillate through chilling machines, which chill and agitate the distillate at the same time.

65. Refrigerating Units.—A suitable refrigerating machine for chilling the wax-distillate is an essential part of wax-plant equipment. These machines may use as refrigerants, carbon dioxide, sulphur dioxide or ammonia, and may be operated as units in compression or absorption refrigerating systems. Carbon dioxide and sulphur dioxide are used in many European refineries for effecting refrigeration, but ammonia is employed almost exclusively in the United States in connection with the absorption system, which is favored over the compression system. The reason for this is that the high-temperature exhaust steam from refinery turbo-sets, used for the generation of electricity, is ideally suitable for low-pressure absorption systems. In ammonia-refrigerating machines, as usually designed, evaporation of liquid ammonia chills a solution of calcium chloride, commonly called brine, which, in turn, cools the oil being pumped through the chillers.

66. Chillers.—The two types of chillers in common use are of the double-pipe and the double-shell type. The double-pipe chilling machine consists of a series, or bank, of concentric

pipes, each connected to the other of the same size, by return bends. The general effect, then, is of a smaller pipe inside a larger pipe, the oil flowing through the inner pipe and the cooling medium through the surrounding space between the inner and the outer pipes. The inner pipe contains a conveyer device for assisting the progress of the chilled and viscous solution through the machine. The conveyers are helicoids, supported on shafts of extra-heavy pipe by means of heavy lugs, to which they are riveted. On the driving end of the machine, driving shafts, projecting through deep stuffing boxes on the end fittings, are fitted to the conveyer. At the other end of the machine, tail-end shafts are similarly fitted. Conveyer bearings inside the machine are so arranged that the conveyer can be readily removed. The chilling-machine is supported on channel-iron stands. A set of outboard bearings is provided to support the outer end of the conveyer driving shafts. To drive the chilling machine, sprockets are fitted to the conveyer driving shafts on which a heavy, link-belt chain runs. Where the size of the refinery permits, these machines make very good interchangers of heat between cold and warm oils. When used for this purpose, they are specially designed.

The double-shell type of chiller resembles a gigantic ice-cream freezer with power-driven paddles so arranged that when they are revolved the resistance of the oil forces the blades firmly against the shell. This prevents the deposition of chilled paraffin on the shell and avoids the insulating effect of such a deposition. Cold brine is circulated between the inner and the outer shells, the transfer of heat from the oil to the brine being through the inner shell.

67. Wax-Plant Operation.—Efficiency in wax-plant operation begins with the preparation, by proper distillation methods, of a wax-distillate cut that will press satisfactorily. In the wax plant the wax distillate usually is cooled first by being passed through coolers in which cold water is used as the cooling medium, then through heat exchangers in which the unpressed wax distillate passes counter-current to the pressed distillate; and, finally, through the chillers proper, where calcium-chloride

solution at a temperature around 0° F. cools the distillate to about 10° to 15° F. Such a procedure will produce a finished oil having a cold test of about 20° to 25° F. The temperature of the distillate leaving the chillers must be kept uniform in order to maintain the same physical characteristics on the finished product.

The cold distillate is now ready for pressing and is pumped into an empty press, the pumping being continued until a hard cake of wax forms on the filter leaves. During the filtering operation, the press is frequently examined from end to end for any leaks that may occur between the rings and plates. If any leaks are located, connections are placed so that the unpressed distillate passes into a space called a cellar. The oil in these cellars is pumped daily, the water settled out and this slop pumped back to the unpressed-oil tank. The rate of flow of the pressed oil is a reliable guide as to when the press is ready to dump. Ordinarily, from 12 to 24 hours is the average time of filtering, depending on the grade of wax being pressed. When the press is ready to dump, the pressure-valve is closed and the pressed-oil trough is pushed to one side. The screw conveyer under the press is turned back in order that any oil in the wax trough around the screw may be carried back into the cellar and not into the wax dump tank. After the trough is clear, the direction of the screw is reversed, so that the wax cakes as dumped will be carried to the dump tanks in the rear, located outside of the press room.

68. Manufacture of Paraffin Wax.—The manufacture of paraffin wax from slack wax, or wax cake, is based on the principle of fractional crystallization. Thus the solid wax cake is gradually heated, as a result of which the oil and low melting-point waxes are gradually run off, leaving a wax of higher melting point and of greater purity. This process is known as sweating the wax. Sweating pans vary in size from about 8 feet wide by 20 feet long to 10 feet wide by 40 feet long, and are of relatively shallow depth. These pans are installed in units of from six to eight pans in a vertical tier, at equal distances apart, and supported by a structural steel frame. The

whole is built inside a substantial brick or concrete chamber or oven, provided at both ends with large, tight-fitting doors that make possible either free circulation or air-tight space as may be desired. About six inches below the top of each sweating-pan and about an inch above the true bottom is fitted a false bottom of 8-mesh galvanized iron or brass screen. This screen is securely fastened to the sides of the pan and further supported on the bottom by means of suitable bracing. Water-circulating coils are installed immediately above the screen. These coils are made up of pipe, usually $\frac{3}{4}$ -inch in diameter, and properly manifolded so as to secure as nearly uniform cooling or heating effect on the charge in the pan as good construction will allow. It is particularly desirable to have uniform heat transference when a hot-water heating system, now quite generally used, is employed. Thermostatic control of the system is a common practice. The melting-down coil is located below the screen. This coil is also usually constructed of $\frac{3}{4}$ -inch pipe. Such an arrangement makes possible the rapid melting of the scale on the screen. This pipe also aids in keeping the screen free from gummy deposits that sooner or later accumulate from the untreated slack wax. Generally, the pan bottoms are self-draining, one or more flow points being installed according to the length of the pan.

69. If the slack wax is dirty, it is washed either with hot water or with a hot, weak-alkaline solution. Sometimes, an acid treatment and subsequent neutralization of the slack wax is necessary. The first step in the sweating operation is that of raising the draining spouts in the pans and then filling the pans with water to the level of the screen. The pans are then filled to the top with hot, melted slack wax, which is subsequently chilled to a temperature at least as low as that of the lowest cut made. Cooling is accomplished partly by exposure of the melted wax to the atmosphere and partly by the cold water circulating through the cooling coils located just above the screen. Atmospheric cooling is hastened by opening all doors, thus providing free circulation of air. The result of the cooling operation is a solid layer of wax, in each pan, which

is ready for sweating, after withdrawal of the water from the pans. The doors are now closed, the building made air-tight and the temperature of the room and of the water passing through the coils is raised gradually, that is, at a rate just fast enough to melt out the oil and low-melting-point wax from the slack wax.

The slack wax contains about 45 per cent. of oil. As the temperature of the sweater is raised, the wax begins to melt and, as it melts, the oil separates and trickles down through the false bottoms. With a further increase in temperature of the sweater, some of the wax is carried off with the oil. Naturally, the impure wax remaining in the pans contains less oil and a higher percentage of pure wax. The operation is continued, several different cuts being made as the temperature in the sweater building is raised, until a product is obtained that contains very little oil. This product is known as crude scale wax. The temperature of the room is now raised to the point at which the crude scale wax will melt and run off the false bottoms, after which this wax is pumped to storage. Foots oil is the name given to the product that first sweats from the slack wax. It usually is pumped to raw wax-distillate storage, re-cracked in fire-stills, and then again recycled through the chillers and pressers. Second and first intermediates are the terms applied to the two wax cuts that follow foots oil in the sweating operation in the order named. Often only one intermediate cut is removed after the foots oil is separated. Crude scale wax and the intermediate cuts are again resweated to obtain sweated wax, and other grades of wax of higher purity than the particular cut being sweated. Some refiners give the crude scale wax, instead of the slack wax, a chemical treatment in order to facilitate subsequent sweating operations. The melting points of commercial grades of paraffin wax vary between 118° and 135° F. The grade of wax desired determines largely the detailed method of conducting the sweating operation.

Sweated wax is given a final purification by filtering through fullers' earth at a temperature above the melting point of the wax, after which it is molded and packed for shipment.

70. Cold-Settling Process.—The residual oil from a paraffin-base crude, or from certain mixed-base crudes that have been chemically treated, may be sold as a steam-refined cylinder stock provided it will flow from a container at average room temperatures; that is, if its cold test or solidification point is not over 75° F. Or, this same stock after filtration through fullers' earth may be sold as filtered cylinder stock. If filtered cylinder stocks of low cold test are desired, the wax must be removed from such oils in the refinery by additional processing operations. Bright stocks are cylinder stocks of low cold test that have been highly filtered. Such stocks are blended with neutral oils to make various grades of motor, engine and machine oils.

Removal of wax from cylinder stocks by cold-settling of a naphtha solution of the oil is being superseded by the centrifugal process. In carrying out the cold-settling process, cylinder stock and light naphtha of about 60 to 62° A. P. I. gravity, but often lower, are mixed together in about a ratio of 60 parts of naphtha to 40 parts of oil, and filtered in solution to the desired color. Or, the oil may be filtered straight or without dilution, and then mixed with naphtha. The mixture of filtered oil and naphtha is then transferred to an insulated tank which is fitted with cooling coils for artificial refrigeration. In this tank the diluted oil is slowly cooled to a temperature of 8° to 10° F., over a four to six-day period of time. The wax, being heavier than the naphtha solution of the oil, falls by gravity to the bottom of the tank. This separation of amorphous wax, or petrolatum, as it is more commonly called, has the effect of lowering the cold test of the reduced oil. Chilling of the oil is stopped when a sample from the tank, upon being reduced, shows the oil to be of satisfactory cold test. The wax-free naphtha solution of the oil is then pumped from the top of the cold-settling tank, and the naphtha is removed from the oil by distillation. Similarly, the petrolatum is pumped from the bottom of the tank and likewise reduced.

71. Sharples Centrifugal Process.—In the Sharples centrifugal process, the oil-naphtha solution is chilled to -10° to

—15° F., over a 48-hour period, the solution being agitated at hourly intervals to keep the wax in suspension. From the chilling tanks the oil is pumped through centrifuges operating at a speed of 15,000 revolutions per minute. Warm water is injected into the machine as a carrier liquid for the removal of the petrolatum. The high speed of the centrifuge greatly increases the difference in gravity between the water, the wax, and the naphtha-oil solution. In this operation the water maintains itself as a flexible carrier in the form of a cylindrical layer on the periphery of the rotor of the centrifuge, and the stiff wax is deposited upon the surface of the water. The water, in turn, continuously conveys the petrolatum from one outlet of the machine, while the wax-free oil issues from another. Thereafter, the operating procedure is similar to that practiced in the cold-settling process.

The Sharples process renders possible continuous operation with the production of bright stocks of lower cold test than can be produced by the cold-settling process. It also makes possible the dewaxing of long residuums; that is, residual oils in which is contained as much of the wax-distillate cut from the crude as is desired. Wax cannot be removed from such oils by cold-settling.

ASPHALT AND MISCELLANEOUS PRODUCTS

72. Asphalt.—Asphalts are solid or semisolid hydrocarbons that either occur as such in nature, or are obtained by refining certain types of petroleum, or are made by combining the two classes mentioned.

The petroleum refiner classifies asphalts as, steam-refined asphalt, blown asphalt, and sludge asphalts, or asphalt pitches.

Asphalt-base crudes are used as the source from which petroleum asphalts are made. Light and heavy Mexican, California, and heavy South Texas crudes are types of crudes that contain a relatively high amount of asphaltic material, and therefore are especially suitable for this purpose.

Steam-refined asphalts are made in a manner similar to that followed in the manufacture of cylinder stocks from paraffin or mixed-base crude oils. In this case, however, asphalt is the

residue remaining in the still, instead of cylinder stock. The lighter distillates are usually removed in a battery of continuous stills, and the residual oil from the last still of the continuous battery is transferred to another still, where it is reduced by batch operation, using much steam, until a maximum still temperature of about 575° to 625° F., is reached. A higher temperature than this is detrimental to the quality of the product. The characteristics of the bottoms depend on the extent of the distillation.

Many of the South Texas crude oils are reduced to asphalt by transferring the residual oil, from which the lubricating distillates have been removed, to stills in which the oil is both air-blown and agitated with superheated steam, while at the same time the still is heated by direct fire. The hydrocarbons that constitute asphalt are decomposed very easily, and for this reason steam is introduced into the still in order to vaporize the volatile constituents at temperatures below their normal boiling points. Hot air is usually employed in blowing the oil. Blowing tends to thicken the asphaltic material in the still. Sulphur is frequently added while blowing, in order to give the finished asphalt certain desired physical properties.

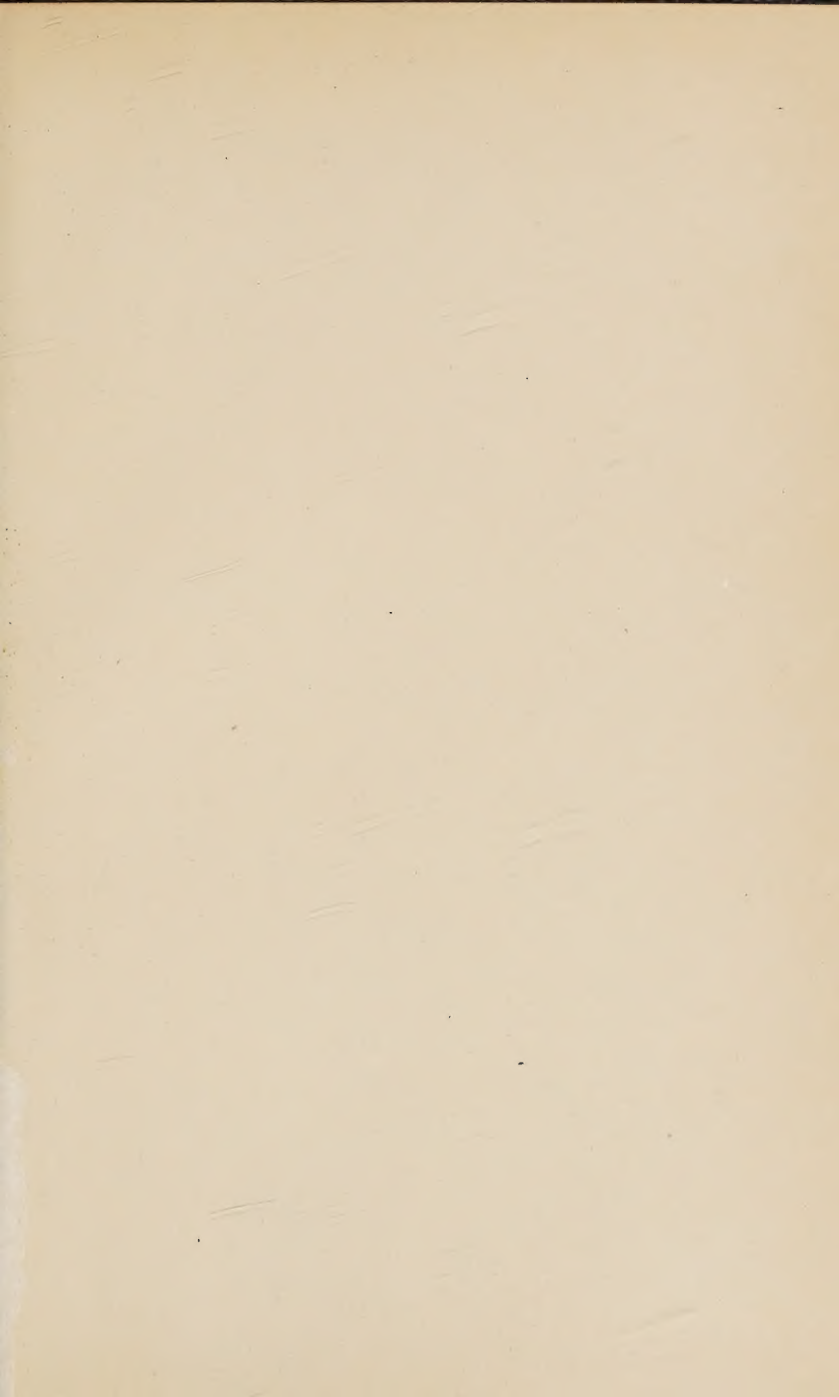
In the case of asphalt made from some mixed-base crudes, such as those found in Mexico, large quantities of superheated steam are usually introduced into the still during the distillation, in order to remove more readily the paraffin hydrocarbons, and thereby increase the ductility of the residuum. Thereafter, this residuum may be blown with air, if a blown asphalt is desired.

Blown asphalts are characterized by their high melting point, low penetration, and the fact that they possess practically no ductility. They are used largely by the roofing trade as coating materials for roofing felts and roofing papers.

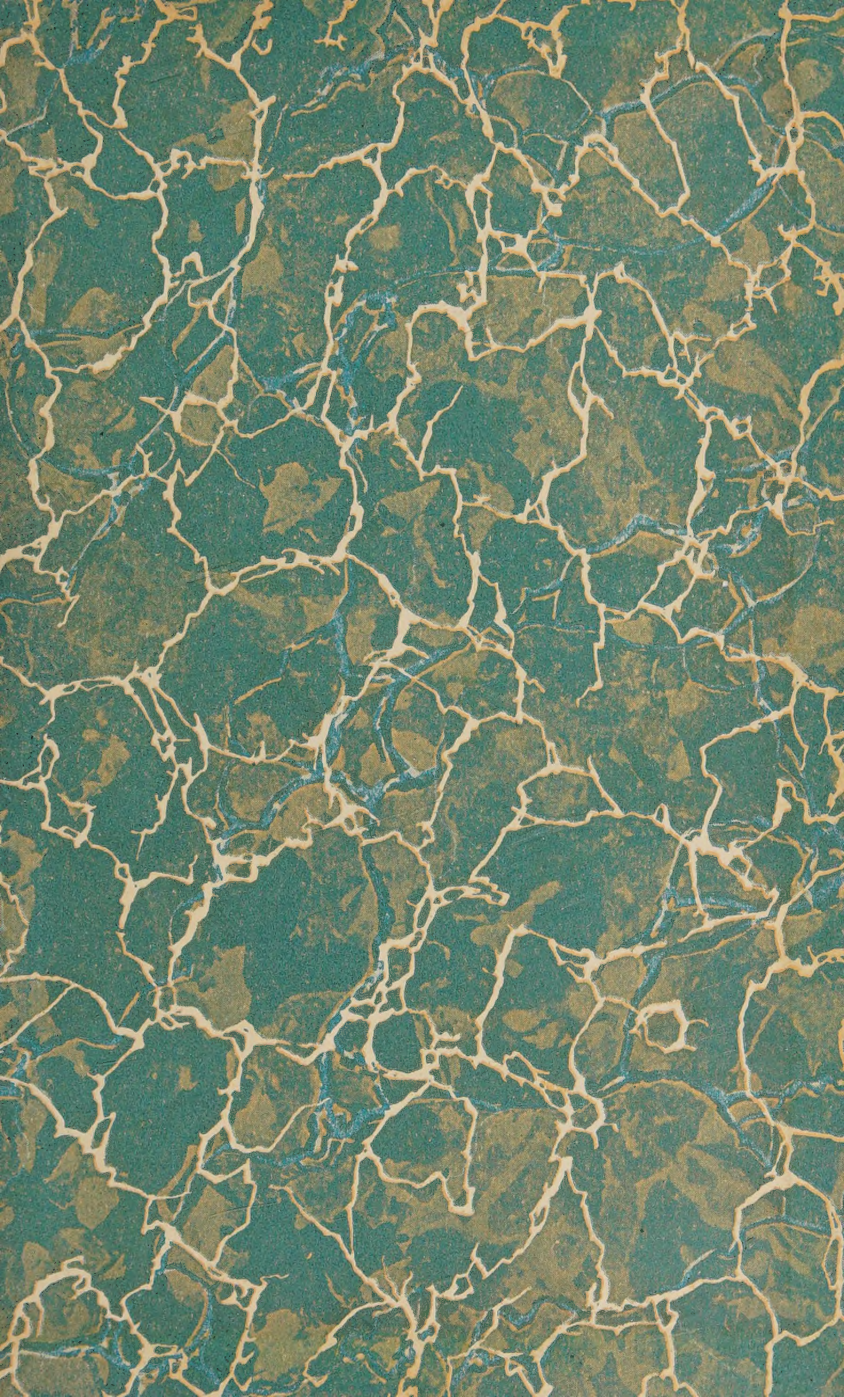
Sludge asphalts are made from the acid sludge that results from the treatment of paraffin distillate and lubricating oils with sulphuric acid.

73. Fuel and Road Oils.—Fuel oil is an indefinite term, properly used to describe any product of petroleum used for

the production of power and heat. It may range from distillates down to and including any residual-oil product that can be made liquid by steam heat and for which there is no better market outlet. Road oil is also an indefinite term covering grades of oil, from distillate down to asphalt that is solid at 60° F., used as a dust preventive. The grade selected depends entirely on the needs of the user and the conditions under which it is to be applied. No special manufacturing procedures are required for making fuel and road oils, other than to blend together oils suitable for use in the finished product to the required physical specifications.









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